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with instruments carefully standardized at the Bureau International at Sèvres.

The analysis was made by a method already used at Harvard[1] for determining sodium sulfate and silver nitrate. About 20 cc. of the solution were removed and weighed; the water was then evaporated and the anhydrous salt remaining was also weighed. An attempt had previously been made to carry out the evaporation in an open platinum basin heated in an oven, but this was found to be quite impracticable, because of spattering. Resort was then had to fused silica flasks of 0.05 liter capacity provided with long necks. Into these the solution was placed, and they were heated to about 103° in an electric oven, while a current of dry air was blown upon the surface of the solution in each. A glass tube, provided with a fused silica cap held in place by a platinum wire, conducted the air down the neck of the flask to within four or five centimeters of the surface of the solution. Any projected particles or drops adhered to this cap. After the water had been driven off, the temperature was gradually raised to 400° and kept there for over two hours, when experiment showed that constant weight was attained. The quartz cap was then detached and dropped into the flask, and after cooling in a desiccator over caustic potash, the flask with its contents was weighed, together with the cap and platinum wire.

An attempt was made to make the dehydration yet more certain by fusing the salt in the quartz flask. With great care this can be done, but the result was sometimes disastrous to the flask, the molten salt attacking the fused silica to a considerable extent. Accordingly, this extreme treatment was abandoned. The fairly constant quantity of water still retained by the salt dried at 400° was probably less than one part in ten thousand, but as it must have been approximately constant in different specimens, no correction was applied for this amount. The loss on fusion, found some time ago by one of us for dehydrated sodium sulfate, was 0.0003 gram from 3.30658 grams of the salt.[2]

The weighings were all made by the method of substitution on a Troemner balance, using standardized weights, and all weighings were reduced to the vacuum standard.

Considerable difficulty was experienced at first in weighing the quartz flasks. Sometimes two hours were needed for the attainment of constant weight, while on other days accurate weighing was impossible. The trouble was probably due, as usual, to three causes, namely, static charges of electricity upon the flask, inequalities in temperature, and humidity.

The first-mentioned difficulty seems to have been the most serious of the three, for after a very small tube containing impure radium chloride in water; and after twenty-three days they were taken out, wiped dry, and left exposed to the air of the room for six hours. The counterpoise was dipped into water for a moment and wiped dry under identical conditions with the other flasks, except as to the length of time of immersion. No change in the relative weights of the flasks was found to have occurred. Hence the silica absorbed no water during its three weeks' immersion. This having been shown, the experiment was repeated, using a sodium sulfate solution containing 11% of the salt. The flasks were kept immersed in this solution for over a month and then washed and weighed. As before, no change in weight was found.

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[1] Richards, *Proc. Amer. Acad.*, **26**, 258 (1891)

[2] Richards and Forbes, THIS JOURNAL, **29**, 813 (1907)

It appears safe, therefore, to conclude that the best quality of fused quartz does not absorb water or sodium sulfate to any appreciable extent when exposed to the action of these substances.

The densities of the floats were determined towards the close of the investigation. Float A was brought into floating equilibrium with the sodium sulfate solution at 20.003°. The density of this solution was ascertained in a large Ostwald pycnometer, of 0.05 liter capacity, provided with ground glass caps and the density of float A was thus found to be 1.10155 at 20°/4°.

From this value, and the appropriate coefficients of expansion, together with the curves to be shortly depicted, the densities of floats C and D were calculated to be 1.10151 and 1.10166. Dividing the weight of each float by its corresponding density, we obtain, as the volumes of the floats, 4.92344, 2.71307 and 4.39704 cc., respectively.

The cubical expansion for fused quartz is often taken as 0.0000018. This is so small as to affect its density only 0.00001 over the range of temperature (4.1°) covered in this research. Assuming the usual value of the coefficient of expansion of glass (0.000025), the volume of glass float D at the lowest temperature (15.9°) is found to be 4.39667 and the density 1.10177, instead of 1.10166, the value at 20°.

These preliminary data having been recorded, the data and curves which show the change of floating equilibrium temperature with concentration of the sodium sulfate solutions may be given. The experiments were begun in January, but the preliminary experiments were affected by the fact that the floats were new and had not attained equilibrium. Hence, for the present purpose these preliminary experiments may be omitted. In the near future we hope to present complete data concerning the slow alteration in volume exhibited by glass and fused quartz on standing as determined in this way; for the method lends itself with especial fitness to this test. The values tabulated are five sets of determinations made in March, 1911. These include all those made during that month except one determination which was vitiated by a known accident.

TABLE.—"FLOATING EQUILIBRIUM" TEMPERATURES OF FLOATS TOGETHER WITH THE CORRESPONDING CONCENTRATION OF SODIUM SULFATE.

Results.

Date of determination.	Float A.	Float C.	Float D.	$\frac{\text{Wt salt}}{\text{Wt solution}}$
Mar. 7	15.888	15.991	.....[1]	0.109322 0.109319
Mar. 9	17.394	17.497	16.910	0.109887 0.109885
Mar. 22	18.408	18.509	18.025	0.110267 0.110267
Mar. 25	19.421	19.516	19.145	0.110670 0.110678
Mar. 28	19.968	20.068	19.729	0.110866 0.110858

The meaning of this table will be made more clear if a single determination is described. A certain solution of sodium sulfate containing nearly 11% of the anhydrous salt was made. On March 9th float A was in equilibrium with this solution under the precautions already stated at the corrected temperature 17.394°; float C at the temperature 17.497°, and the glass float D at 16.910°. When these temperatures had been satisfactorily determined, two portions of the solution were weighed out in quartz flasks. Of these portions, one weighing 20.1283 grams yielded 2.21184 grams of dried sulfate, and another weighing 20.1471 grams yielded 2.21387 grams of solid. The percentage of sodium sulfate present in the solution was thus found to be 10.9887 and 10.9885 by the two determinations, respectively, as given in the last column of the table. The difference between them corresponds to 0.04 milligram, which is about the probable error of weighing. Some of the pairs agreed more closely; others less closely, but it was clearly possible to determine the concentration of the solution with great accuracy. As already stated, the chief uncertainty lay in the question as to whether or not the salt was wholly dry, on account of the inexpediency of fusing this substance in a quartz flask. A platinum flask would have served better.

The results, when plotted with regard to concentration and temperature, give two almost linear parallel curves for the two quartz floats. The glass float also gives almost a straight line, but its greater alteration in volume with change in temperature is indicated by the increased slant towards the temperature axis as compared to the curves given by fused silica. The fact that these curves are so nearly straight is very fortunate as regards the application of the method to the calibration of thermometers; for very few points are needed to fix the line throughout its length.

The method of using either of these curves for standardizing a thermometer is as follows: The particular float chosen or one constructed of similar material and of nearly the same average density, is placed in a solution of sodium sulfate maintained at the lower of the temperatures to be verified. A weaker or more concentrated solution of sodium sulfate is added at this constant temperature until the float is in precise floating equilibrium. Some of the solution is then removed and put on one side for analysis. Immediately afterwards the solution is warmed to the other end

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[1] Below the graduation of the thermometer.

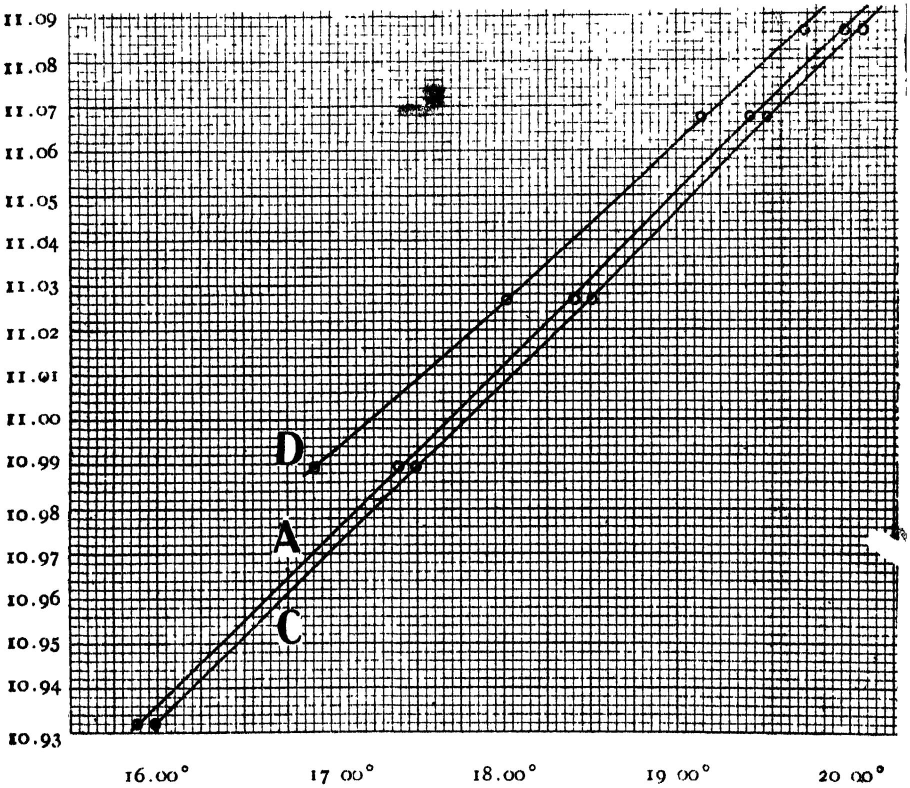

Fig. 2.—Curves showing relation of floating equilibrium temperature to concentration of solutions for three floats: A, C (silica) and D (glass)

of the temperature-interval under investigation; floating equilibrium is again attained by increasing the concentration of the sodium sulfate, and a new portion is taken out for analysis. The two points on the curve corresponding to these two percentage compositions of solution should give the true temperatures; and the corrections of the thermometer employed are simply found by subtracting its readings from the two values thus read off from the curve.

For example, let us suppose that with a given thermometer and a similar glass float, the temperature 17.200° was found to correspond exactly with

11.0000% of dissolved sodium sulfate, whereas the temperature 18.200° was found to correspond to 11.0325%. The temperatures (as found from a much enlarged curve or by interpolation) which ought to have corresponded to these concentrations were, respectively, 17.244° and 18.195°. Accordingly, the thermometer read 0.044° too low on the lower point and 0.005° too high on the upper point. Instead of being exactly 1.000°, the true temperature-interval was, therefore, the difference between the two last-given figures, namely, 0.951°.

Evidently, in order to attain the certainty of 0.001°, very great accuracy in analysis is necessary. A variation of 0.01° in temperature corresponds to only about 0.0034% of the weight of salt in the solution, or 0.06 milligram when only two grams are weighed. Of course, the curve as given above, is nothing but a preliminary one, and serves rather merely to exemplify the method than to act as a final standard of reference. The technique may clearly be much improved. The line, as drawn, is not perfectly smooth; the irregularity may be due either to an imperfect analysis of the solution taken from either of the two upper series of points, or to an error in the thermometer employed at one of these positions. Such irregularities are not inherent in the method but may be traced to their source through further experiment. For finality, many more determinations should be made with a number of thermometers standardized independently with the greatest care at the Bureau International, and, moreover, floats of definite materials should be employed so that the standard may be easily duplicated in any given locality at any given time. In the near future, experiments are to be made here with a variety of such floats, for example, of platinum, silver and glass of definitely known composition. Besides this, solutions of other substances, especially hydrochloric acid, are to receive attention.

Nevertheless, even without further knowledge, a single curve of this sort may be useful in comparing one part of a given thermometer with another part, or in smoothing out irregularities in a curve giving its corrections. If a smaller degree of precision, than that aimed at in the present work is sought, the analysis may be carried out volumetrically, and the problem becomes vastly easier.

It is evident that, when the locus of a given curve over a definite interval has been once for all obtained, any similar float may be standardized by means of a very few points. For example, if a small range were concerned, the two points recently found at Harvard for the transition temperatures of sodium chromate, namely, the decahydrate-hexahydrate, 19.525°, and the decahydrate-tetrahydrate, 19.987°, might be used; or for a larger range these points in conjunction with the transition temperature of sodium sulfate, 32.383°.

If sufficient care is employed, this method may also be used for determining the coefficients of expansion of liquids with known floats, or coefficients of expansion of floats with known liquids. Therefore, any substance which may be made into a float may profitably be studied as to its coefficient of expansion in this way; and such studies will be made in the near future in the Wolcott Gibbs Memorial Laboratory.

The authors take pleasure in expressing their gratitude to the Carnegie Institution of Washington for generous help in the prosecution of this work.

Summary.

In this preliminary paper, experiments are described showing how the phenomenon of floating equilibrium may be used to standardize thermometers. The method consists in determining the temperatures, at which different analyzed solutions of a given substance attain exactly the density of a given float. When the almost linear curve, showing the relation of this floating equilibrium-temperature to percentage composition, has once been established, it will serve for the calibration of any thermometer at any time.

The use of the method as a convenient means of determining the coefficients of expansion of liquids with known floats, or coefficients of expansion of floats with known liquids is also indicated.

Further work upon the subject is now being prosecuted in the Wolcott Gibbs Memorial Laboratory of Harvard University.

[Contribution from the Chemical Laboratories of New Hampshire College.]

THE DIMETHYL PHOSPHATES OF THE RARE EARTHS.

By J. C. Morgan and C. James.

Received November 8, 1913.

The study of methods for the separation of the rare earths, and of new compounds of the rare earths that seem likely to be of use for such purposes, has, for a long time, occupied the attention of those interested in this branch of chemistry.

The rare earth salts of dimethyl phosphoric acid seemed, on preliminary investigation, to be possessed of properties which would make dimethyl phosphoric acid an extremely valuable reagent for the separation of some of the rare earths. Therefore, a study of the properties of these compounds was commenced.

This investigation involved the preparation of dimethyl phosphoric acid; the preparation of the rare earth compounds from this; the determination of the composition and solubility of these compounds; and finally several fractionations of rare earth mixtures.

Preparation of Dimethyl Phosphoric Acid.—This acid was prepared, according to the method of Hugo Schiff,[1] by allowing methyl alcohol to drop slowly into phosphorus oxychloride. About 200 cc. of phosphorus oxychloride were placed in a liter flask and 250 cc. of methyl alcohol were added, drop by drop, through a separatory funnel fitted to the flask. During the reaction, the flask was shaken in a stream of cold water and the temperature maintained between 25° and 30°. The large quantities of hydrochloric acid gas and methyl chloride which were evolved, passed off through a side tube. At the completion of the reaction, which required from an hour to an hour and a half, there remained a colorless, somewhat syrupy liquid, consisting of both dimethyl phosphoric and phosphoric acids with some hydrochloric acid and methyl chloride. This was removed to an evaporating dish and heated upon the steam bath until the hydrochloric acid and methyl chloride were expelled. The syrupy acids were then diluted and neutralized with barium carbonate. The phosphoric acid was removed as barium phosphate. The precipitate was filtered off, leaving a clear filtrate consisting of a solution of barium dimethyl phosphate, together with traces of barium monomethyl phosphate. This solution was treated with just sufficient sulfuric acid to precipitate all the barium as the sulfate, which after digestion at 95° was removed by filtration, leaving a clear solution of dimethyl phosphoric acid.

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[1] *Chem. Centralblatt,* 1857, 761–763, 864.

Yttrium Dimethyl Phosphate.—This salt was obtained by dissolving yttrium hydroxide in dilute dimethyl phosphoric acid. After stirring for some time, the liquid became clear. The solution was then filtered and placed upon a water bath, the temperature of the latter being kept at about 90°. This treatment caused a quantity of crystalline yttrium dimethyl phosphate to form. The precipitate was filtered off and washed with boiling water. The compound was next dissolved in as small an amount of water as possible, and permitted to crystallize by spontaneous evaporation. Groups of white needle-like crystals, radiating from a common center, were formed. These were removed, dried between filter papers, and then placed in an oven at 100° for four hours. The results of the analysis seemed to show that a very small amount of water was retained. Further drying at the same temperature failed to make any difference.

Yttrium dimethyl phosphate dissolves in water at 25° to the extent of 2.80 parts of the anhydrous salt to 100 parts of water. At 95° only about 0.55 parts dissolve in 100 parts of water.

Calculated: Y_2O_3, 24.34; found: 24.06.

Lanthanum Dimethyl Phosphate.—This substance was prepared by dissolving the oxide in dilute dimethyl phosphoric acid. The solution, after filtration, was concentrated upon a water bath until a skin began to form upon the surface, after which it was permitted to crystallize by spontaneous evaporation. The resulting crystals were dissolved in water and recrystallized once again by spontaneous evaporation. These crystals were separated from excess of mother liquor by pressing between filter papers and finally dried in air.

Lanthanum dimethyl phosphate forms white hexagonal crystals. One hundred parts of water dissolve 103.7 parts of the anhydrous salt at 25°. The solubility at 100° did not vary like that of the other rare earths. The solubility at 95° appeared to be somewhat difficult to determine, owing to the fact that the solution had a tendency to become colloidal.

In order to determine the phosphorus, a weighed sample of lanthanum dimethyl phosphate was first fused with sodium peroxide to oxidize the methyl groups and get the phosphorus present as phosphate. The usual method was then followed.

Calculated: La_2O_3, 29.63; P_2O_5, 38.75; found: La_2O_3, 29.45; P_2O_5, 38.63.

From the above analysis, it was considered that the compound contained four molecules of water of crystallization, as shown by the formula: $La_2[(CH_3)_2PO_4]_6.4H_2O$.

Cerous Dimethyl Phosphate.—The cerous compound was obtained by treating cerous carbonate with a dilute solution of the acid. The clear solution was evaporated on the water bath until a skin began to form upon the surface, as was observed in the case of the preceding substance. It was further concentrated by spontaneous evaporation. The crystals obtained in this manner were again crystallized from water.

Cerous dimethyl phosphate is a white crystalline solid belonging to the hexagonal system. It is very soluble in cold water, but less soluble in hot. One hundred parts of water dissolve 79.6 parts of the anhydrous salt at 25°, and about 65 parts at 95°. Upon analysis 33.08% CeO_2 was found. This still remained after drying for some time at 100°, and corresponded to the formula: $Ce_2[(CH_3)_2PO_4]_6.H_2O$.

Praseodymium Dimethyl Phosphate.—A solution of this dimethyl phosphate was prepared by dissolving praseodymium oxide in the acid. The liquid was concentrated on the water bath until small crystals began to form, after which it was set aside to evaporate at ordinary temperatures. The compound, purified by recrystallization, formed green, hexagonal crystals. 64.1 parts are dissolved by 100 parts of water at 25°

Neodymium Dimethyl Phosphate was prepared in a similar manner to the praseodymium compound. It forms pale lilac-colored hexagonal plates. At 25°, 56.1 parts dissolve in 100 parts of water, while at 95°, only about 22.3 parts are dissolved by 100 parts of water. An analysis showed the presence of 32.27% of Nd_2O_3, thus pointing to the formula: $Nd_2[(CH_3)_2PO_4]_6$.

Samarium Dimethyl Phosphate.—A small quantity of the acid was neutralized with samarium oxide. The solution thus obtained was concentrated on the water bath until nearly solid, owing to the formation of the dimethyl phosphate crystals. It was filtered while still hot. The salt was dissolved in water and crystallized by evaporation at ordinary room temperature.

Samarium dimethyl phosphate forms cream-colored hexagonal prisms. One hundred parts of water dissolve 35.2 parts of the salt at 25° and about 10.8 parts at 95°. 33.11% Sa_2O_3 was found to be present, indicating no water of crystallization like most of the rare earth dimethyl phosphates.

Gadolinium Dimethyl Phosphate was separated from its solution by carefully heating.

It forms white, needle-like crystals very similar to the yttrium compound. One hundred parts of water dissolve 23.0 parts of the salt at 25°, while only 6.7 parts are dissolved by the same quantity at about 95°. The compound contained 34.00% Gd_2O_3.

Erbium Dimethyl Phosphate was prepared in a similar way to the ytterbium salt described below.

It forms very pale-colored needles, 1.78 parts dissolving in 100 parts of water at 25°.

Ytterbium Dimethyl Phosphate.—The ytterbium oxide was dissolved in a slight excess of hydrochloric acid, and the solution diluted considerably. A sufficient quantity of dimethyl phosphoric acid to react with the ytterbium present was neutralized with sodium carbonate, and then made slightly acid with a few drops of dimethyl phosphoric acid. This solution was diluted and slowly added to the ytterbium chloride with careful stirring. A precipitate of ytterbium dimethyl phosphate formed, which slightly increased in amount on heating the solution to 100°. The precipitate was filtered off, dissolved in cold water, and again precipitated by heating. The white needle-like crystals dissolve to the extent of 1.2 parts per 100 parts of water at 25°. Only 0.25 is dissolved by 100 parts of water at about 95°. An analysis showed 35.73% Yb_2O_3, which corresponds to the amount contained in the formula of the anhydrous substance.

TABLE OF SOLUBILITIES OF DIMETHYL PHOSPHATES.

Element.	Crystal form.	Parts of salt per 100 parts of water at 25°.
Lanthanum	Hexagonal crystals	103.7
Cerium	Hexagonal plates	79.6
Praseodymium	Hexagonal plates	64.1
Neodymium	Hexagonal plates	56.1
Samarium	Hexagonal prisms	35.2
Gadolinium	Long needles	23.0
Yttrium	Long needles	2.8
Erbium	Long needles	1.78
Ytterbium	Long needles	1.2

Fractionation of Material.—Since, as already stated, the study of new compounds of the rare earths is carried on mainly to obtain compounds adaptable to a more complete and more rapid separation of these elements, no study would be complete without determining the behavior of mixtures of the dimethyl phosphates. Several fractionations were conducted, and the method employed was that of precipitation by heat. In the case of the less soluble compounds, a dilute solution was prepared. The beaker containing this solution was then placed in a water bath and the temperature of the bath gradually raised, the solution being constantly stirred. As soon as a fair amount of precipitate had formed, the liquid was filtered off and the precipitate retained as Fraction I. The filtrate was again heated until another lot had separated, and again filtered. The dimethyl phosphates collected from this second heating were put aside as Fraction II. In this manner fractions were taken up to and inclusive of 95°. Additional fractions were obtained by fractionally evaporating the mother liquor.

These fractions were further fractionated by dissolving the least soluble fraction in water, and heating in the water bath to the temperature at which Fraction I was removed. The precipitate which had formed at this point was removed by filtration and retained as Fraction I 2. The filtrate was used to dissolve Fraction II, and the solution heated as before to the temperature of removal of Fraction II. The precipitate was taken as Fraction II-2, and the filtrate used to dissolve Fraction III. By proceeding in this manner any degree of fractionation, which was desired, could be obtained.

During, and at the completion of the fractionation, various fractions were examined with regard to color of oxide, nitric acid solution, and spectrum.

Gadolinium Material.—A material, containing gadolinium with only sufficient traces of terbium to color the oxide orange-brown, was first submitted to fractionation with dimethyl phosphoric acid.

The oxide of this crude gadolinium was dissolved by stirring with the acid until all had dissolved. The liquid was then treated as described above.

The fractions were taken as follows: Fractions I, I–2, I–3 at 65; Fractions II, II–2, II–3 at 90°; Fractions III, III-2, III–3, after evaporating the mother liquor from Fractions II to one-half volume; and Fractions IV, IV–2, IV–3, upon complete evaporation.

A fair idea can be formed, with regard to the rapidity of the method, by observing the change in color of the oxides. The oxide from Fraction II was of a dark brown color, that of Fraction IV light brown, and that of Fraction IV–3 pale cream.

This showed a rapid concentration of the gadolinium in the most soluble fractions, while the impurity—terbium—collected in the least soluble.

It is interesting to note that this fractionation required only about forty-eight hours to give a comparatively pure gadolinium. This shows a great increase in the rapidity of the separation over all previous methods.

Fractionation of Yttrium Material.—The next oxides consisted of a mixture of those of yttrium, holmium and dysprosium with traces of erbium, samarium, gadolinium, terbium, neodymium and praseodymium. They were dissolved in hydrochloric acid, the solution diluted and boiled with an excess of sodium hydroxide. The precipitated hydroxides were filtered off and washed with hot water until free from chlorides and dissolved by stirring with the dilute dimethyl phosphoric acid. The resulting solution was then submitted to the usual fractionation.

Fraction I was removed at 38°, Fraction II at 48°, Fraction III at 65°, Fraction IV at 96°, while Fractions V, VI, VII and VIII were taken by fractionally evaporating the mother liquor from Fraction IV.

Fraction I.—The oxide was yellowish, and the absorption spectrum showed a rapid concentration of erbium. Holmium and dysprosium were also present.

Fraction II.—This portion gave a yellowish colored oxide. The spectroscope showed holmium and dysprosium with very small quantities of erbium.

Fraction VI.—The oxide was colored an orange-brown. An intense absorption proved the presence of very much dysprosium, less holmium, and the merest possible trace of neodymium.

Fraction VII.—Reddish brown oxide. The absorption spectrum was very weak, showing the presence of a small amount of neodymium and traces of samarium and dysprosium. The green band of holmium could barely be detected.

Fraction VIII.—This gave an orange-brown oxide. The spectrum showed intense absorption bands, indicating the presence of a large quantity of neodymium, a very little praseodymium, and only a trace of samarium.

Fractionation of a mixture of earths, from monazite, giving more soluble double sulfates. The earths present consisted largely of gadolinium and dysprosium with small amounts of terbium, holmium and neodymium.

The oxides were warmed with dimethyl phosphoric acid until entirely converted into dimethyl phosphates, after which the thick mass was stirred with water until dissolved.

The fractions were collected as follows: Fractions I to III up to 95°; and Fractions IV and V by evaporation of the mother liquor from Fraction III.

Fraction I gave a brownish yellow oxide, which, when dissolved in nitric acid, gave a yellowish green solution. With the aid of the spectroscope, it was found that large amounts of dysprosium were present, accompanied by a little holmium.

Fraction II.—The oxide was chocolate-brown. Its nitrate solution was faintly green and showed weak absorption bands of dysprosium and terbium.

Fraction V.—Oxide red-brown. Absorption spectrum indicated very small quantities of neodymium and dysprosium.

It will be observed from the above fractionations that the rate of separation of the rare earths is vastly greater than practically all the methods given up to the present time. Lanthanum, cerium, praseodymium, neodymium are left at once in the mother liquor. Samarium, europium, and gadolinium are much less soluble than those previously mentioned, while they are more soluble than terbium, dysprosium and holmium. Erbium, thulium, yttrium, ytterbium, etc., collect in the least soluble portions.

Since the solubilities of these compounds are the reverse of the usual type, they may be used for the rapid purification of many of the rare earths. For instance, we can easily remove traces of neodymium from samarium by this means, as the samarium dimethyl phosphate separates before the neodymium compound.

It is necessary to state that there is some inconvenience when working with the salts of dimethyl phosphoric acid, since they undergo a very gradual decomposition. A gelatinous precipitate is formed, very slowly, in the case of the rare earths, which filters with difficulty.

DURHAM, N. H.

THE UTILIZATION OF DIFFUSION PROCESSES IN THE PREPARATION OF PURE SUBSTANCES.

BY JOHN JOHNSTON.

Received October 27, 1913.

The possibilities of utilizing diffusion processes in preparing certain substances in the form of relatively large crystals appear to be much less widely known than they deserve to be, in view of the simplicity of the procedure and the purity of the resultant product. This type of method is quite generally applicable; its use is especially advantageous in the formation, by precipitation, of sparingly soluble substances. Such substances, as ordinarily prepared, tend to separate out in very fine powder which, by reason of its large extent of surface, often contains much absorbed material, in which case they are extremely difficult to purify satisfactorily. By allowing the solutions to mix by the operation of diffusion we may ensure very slow precipitation, and in this way obtain large, well-developed crystals, which can easily be washed free from any adherent foreign material.

The size of grain of a precipitate *AD* (*e. g.*, $Ca(OH_2)$)), formed by the interaction of solutions *AB* and *CD* (*e. g.*, $CaCl_2$ and NaOH), depends upon the virtual concentration in the mixed solution of the ions A^+ and D', relative to their concentrations in the solution which, under the conditions of experiment, is saturated with respect to *AD*. This was demonstrated directly by von Veimarn for precipitates of barium sulfate;[1]

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[1] P. P. von Veimarn, *Z. Chem. Ind. Kolloide*, 2, 3.

and all available lines of evidence substantiate its general applicability. In other words, the fineness of grain is determined by the virtual and momentary degree of supersaturation of the substance *AD* in the mixed solution. Indeed, the truth of this is apparent from general principles, for a high degree of supersaturation is obviously most readily dispersed by the precipitation of a large number of particles, consequently by the formation of very fine particles. Moreover, growth of larger particles will occur only if the degree of virtual supersaturation is so low that the rate of deposition from the solution does not exceed a certain maximum characteristic of the particular crystal.

The formation of large particles of slightly soluble substances, therefore, is favored: (1) by causing the separation of the substance to proceed very slowly; (2) by so choosing the temperature and composition of the medium as to have the substance as soluble as possible. Moreover, the average size of grain of a precipitate is increased when it remains in contact with a medium in which it is soluble at all, because a solution saturated with respect to the larger grains is unsaturated with respect to the smaller.[1] Advantage can be taken of all of these favorable factors by making use of a process in which mixing of the reacting solutions is effected by diffusion.

Such diffusion methods were used many years ago by Daubrée and others of the French school, in their work on the artificial production of minerals. They generally placed the reacting solutions in two vessels connected by some sort of siphon—a glass tube or a wick; but this procedure has the disadvantage that precipitation takes place within the siphon and closes it up. It is much better to allow each of the solutions to diffuse separately into a large volume of liquid within which they come together slowly and react. The choice of liquid depends upon the solubility of the substance, being either a saturated solution of the substance (*AD*), or water alone, or a solution containing some foreign substance which increases the solubility of *AD* but at the same time does not separate out along with it as a solid double salt.

To carry out such a process the easiest way is to fill up with appropriate liquid a large vessel at opposite sides of which two small evaporating dishes[2]—one containing the solid *AB*, the other *CD*—are carefully placed; the whole is left in some place not exposed to violent temperature fluctuations, in order to eliminate the disturbing effects of convection. In this way, beautiful crystals of calcium hydroxide formed by interaction of calcium chloride with sodium hydroxide in a large desiccator (24 cm. diameter, capacity about 6 liters) in about 3 weeks at room temperature; the crystals thus formed being hexagonal prisms, with the base about 1 mm. thick and 2–3 mm. long.[1] Similar experiments carried out at 100° yielded fine crystals of barium sulfate,[2] 1–2 mm. long, which were, within the unavoidable error of the determination, free from the occluded material carried down by barium sulfate when it is precipitated in the ordinary way. In carrying out experiments of this kind at temperatures other than room temperature, it is a matter of considerable difficulty to prevent premature mixing by convection at the moment when the components are introduced. To surmount this difficulty, recourse may be had to the following modified procedure, illustrated in the figure, the principle of which is that the component solutions siphon very slowly into the medium:

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[1] Just as small liquid drops are unstable in presence of larger drops, by reason of the greater vapor pressure of the former.

[2] It is advisable that the upper edge of these vessels be sensibly horizontal; otherwise, flow may take place over the lowest point of the rim.

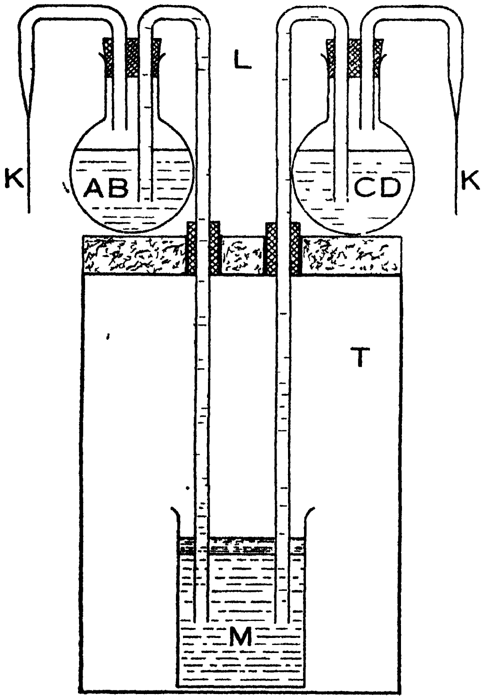

Diagram of arrangement for securing slow mixing at 100° of the component solutions (*AB* and *CD*). *T* is the steam bath, *M* the vessel containing the main mass of liquid, evaporation of which is prevented by a layer of paraffin wax. The rate of transfer of the solutions down through the siphons *L* is regulated by the entrance of air through the extremely fine capillary tubes *K*.

Into the main mass of liquid[3] dip two tubes, each of which serves as a siphon for the transfer of one of the component solutions; the latter are contained in stoppered flasks placed, if desirable, outside of the temperature bath. These siphon tubes are not constricted, because they choke up very soon if they are narrow enough to be effective for the purpose in hand; but a very slow transfer of each solution is secured by allowing air to enter each of the flasks only through a second tube which is drawn out to an exceedingly fine capillary. It is somewhat difficult to draw down two such capillaries, so as to obtain equal rates of flow; this may be helped by adjusting the concentrations of the two solutions.

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[1] A crystallographic description of these crystals will be published elsewhere.

[2] J. Johnston and L. H. Adams, This Journal, 33, 834 (1911).

[3] Evaporation of this liquid is readily prevented by a floating layer of paraffin.

It may be remarked that, in spite of a long and varied series of diffusion experiments, we have been unable to prepare magnesium hydroxide in good crystals, presumably because the actual rate of diffusion was still not small enough in view of the limiting saturation of this substance. Similar attempts with silicates resulted in the separation of colloidal material only; this may be due to hydrolysis, or to the insolubility of the silicate, or to both of these factors. The only possibility of increasing the saturation limit in this case would seem to be increase of temperature; and it is very doubtful if this would avail much, since the indications are that silicates are still very sparingly soluble in water even at temperatures of 360° or higher. A few trials made at 200° in a small autoclave were unsuccessful; indeed the experimental difficulties in the way of securing sufficiently slow mixing at temperatures above 100° are very great, so that we abandoned attempts to prepare crystalline silicates in this way.

Nevertheless, it is probable that, by means of diffusion experiments as described above, one may prepare good crystals of many sparingly soluble substances, which otherwise cannot readily be obtained except as very fine powder, usually more or less contaminated with occluded material. The slowly formed crystals obtained in this way are practically free from impurity and hence constitute first-rate material with which to undertake physico-chemical determinations, such as measurements of solubility. The use of this type of material for such purposes would doubtless yield quite definite and reproducible results which would, with advantage, replace some of the present uncertain data.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
October, 1913.

A NEW METHOD FOR THE PREPARATION OF COLLOIDAL FERRIC HYDROXIDE.

BY THEODORE COHEN.

Received November 3, 1913.

Many of the methods already in use for the preparation of soluble ferric hydroxide are based upon the hydrolysis of a ferric salt. The soluble ferric hydroxide thus formed is held intact without any appreciable evidence of the settling of the solid phase, after standing for some time. A typical reaction of this kind takes place when a molar ferric chloride solution is neutralized with a molar ammonium carbonate solution. If the liquid thus obtained is filtered and then dialyzed, ferric hydroxide will be obtained in the colloidal state, brought about through the hydrolysis of the ferric salt, according to the main reaction:[1]

$$FeCl_3 + 3HOH = Fe(OH)_3 + 3HCl.$$

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[1] A. A. Noyes, THIS JOURNAL, **27**, 94 (1905).

The writer claims another method for preparing colloidal ferric hydroxide, due to the hydrolysis of an iron salt, ferric nitrate, which hydrolysis takes place in a nitric acid solution, containing free reacting copper. A careful research through the available chemical literature gave no account of the preparation of colloidal ferric hydroxide according to the method which is described below.

While working with a copper sulfate solution, in which was immersed an iron nail, dilute nitric acid was accidentally added in excess. A violent reaction took place, brownish fumes were evolved (liberation of N_2O_4, nitrogen peroxide) and at the end of the reaction, a reddish yellow mixture was obtained. This was filtered several times, the liquid passing through the filter paper unchanged, and viewed by transmitted and reflected light. In the former case, the color was deep red, but in the latter, a distinct reddish yellow opalescence (probable presence of a colloid) could be readily seen. A drop of concentrated sulfuric acid was added, when a red-brown gelatinous precipitate immediately appeared. This precipitate was found, upon analysis, to be ferric hydroxide. Another portion of the liquid was placed in a U-tube and an electric current sent in. A red gelatinous mass appeared on the cathode and when analyzed was also found to be ferric hydroxide. Concluding that a colloid was probably present in solution, and that the presence of copper influenced its formation, the following experiments were carried out:

(1) Three grams of iron (nails) were placed into 10 cc. concentrated nitric acid in a large test tube. No reaction took place. This would be expected, since concentrated nitric acid renders the iron passive.

(2) Three grams of iron (nails) were placed in 10 cc. concentrated nitric acid in an Erlenmeyer flask and a small piece of sheet copper was added at the same time. No action occurred but when diluted with a little water, immediate violent action took place. At the conclusion of the reaction, a dark red liquid was obtained which was filtered and dialyzed to remove electrolytes. (*a*) A 10 cc. portion was treated with concentrated sulfuric acid, when immediate coagulation took place. (*b*) Another portion was placed in a U-tube and a current of 110 volts passed in. A gelatinous red precipitate collected on the cathode. (*c*) Still another portion was treated with electrolytes of varying concentration and in each case coagulation took place, with increased speed as the concentration of the electrolytes increased. Electrolytes having anions of high valence were still more effective in producing coagulation than those having low valence anions. The facts that sulfuric acid, other electrolytes and the electric current precipitated ferric hydroxide, verify its original colloidal nature. The collection of the precipitate around the cathode proves the colloid to have a positive charge. Such is known to be the case with true colloids of ferric hydroxide.

(3) Three grams of iron (nails) were placed in dilute nitric acid, specific gravity 1.20, and allowed to react. A slight brownish solution was obtained. The addition of sulfuric acid failed to produce coagulation; there was simply a change in color to pale green, as would be expected of ferric salts when they are treated with sulfuric acid. At times, in the above case where copper was absent, a slight precipitate appeared upon the addition of sulfuric acid. This was probably due to the slight hydrolysis of the ferric salt, giving soluble ferric hydroxide, which would be precipitated by the addition of sulfuric acid.

Another set of experiments was carried out with iron as filings, containing copper as an impurity. Colloidal ferric hydroxide was also obtained.

(1) Two grams of iron (filings) were added to 5 cc. concentrated nitric acid in an Erlenmeyer flask. No action took place. Water was added from a buret until the reaction started. A brownish red, curdy, gelatinous mass was left, which went into solution on the addition of water. This was filtered and dialyzed, when a yellow-brown liquid was obtained, which showed distinct opalescence.

(2) Three grams of iron (filings) were placed in 5 cc. concentrated nitric acid and then diluted. Reaction began and the resulting liquid was filtered and dialyzed. Opalescence was clearly visible.

(3) Three grams of iron (filings) were added to 10 cc. concentrated nitric acid and diluted The mixture was filtered and dialyzed when a deep, ruby- or blood-red liquid was obtained. In this case, the color was deeper red than in the two previous experiments. The acid when diluted in each case had a specific gravity about 1.20. Each solution showed distinct opalescence and a drop of sulfuric acid or the electric current caused coagulation with the separation of ferric hydroxide. These tests again verify the colloidal nature of the ferric hydroxide. Mixtures thus prepared have remained since April without the least evidence of the settling of the solid phase, ferric hydroxide.

However, when 1 gram of iron filings was added to concentrated nitric acid, diluted, and then filtered at the end of the reaction, a clear yellow-brown filtrate was obtained; the addition of sulfuric acid :u faile to produce any coagulation.' This may perhaps be due to the ext ce'of nitric acid in the solution, which would tend to drive back the hydrolysis completely, in the case of the nitrate.[1]

$$Fe(NO_3)_3 + 3H_2O \rightleftarrows Fe(OH)_3 + 3HNO_3.$$

Having obtained a colloid with iron filings which were known to contain copper, iron, reduced by hydrogen, was placed into dilute nitric acid. This solution gave no test for colloidal ferric hydroxide; but when a similar portion was placed into concentrated nitric acid, containing a small piece of copper, and then diluted, the colloidal ferric hydroxide which was produced was precipitated upon the addition of a drop or two of concentrated sulfuric acid.

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[1] A. Smith, "Inorganic Chemistry," 1912, p. 755.

Since iron, copper, water and nitric acid are the chief constituents, the main reaction which produces the colloid could be expressed by an equation,

$$\begin{array}{lcll} Fe(NO_3)_3 & \rightleftarrows & Fe^{+++} & + \; 3NO_3^- \\ 3HOH & \rightleftarrows & 3OH & + \; 3H^+ \\ & & \downarrow\uparrow & \quad\;\; \downarrow\uparrow \\ & & Fe(OH)_3 & \;\; 3HNO_3. \end{array}$$

The formation of soluble ferric hydroxide, brought about by the hydrolysis of the ferric nitrate in the solution, must have been favored in some manner, by the presence of the copper.

As shown by the second equation, the presence of nitric acid would drive back the hydrolysis of the ferric salt completely. Reasoning upon this fact led to the conclusion that the ferric hydroxide formed as a result of hydrolysis would remain as such, if the effect of the nitric acid could be destroyed. With this in view the following experiments were carried out:

(1) A concentrated solution of ferric nitrate was boiled for a considerable time, when the yellow-red original color of the solution became deep red. Upon cooling, however, the deep red returned to its original color, and sulfuric acid gave no trace of colloidal formation. This would be expected, since the nitric acid formed would reverse the reaction, as already indicated.

(2) Another boiling solution of ferric nitrate was treated with copper filings and a deep blood-red solution was obtained. This was filtered and allowed to cool but the deep blood-red color still remained. The addition of sulfuric acid gave a heavy precipitate of ferric hydroxide, and further tests verified the presence of cupric nitrate in the solution. Copper having combined with the nitric acid, the ferric nitrate could then hydrolyze. Cooling would have no effect since the reversing power of the acid was destroyed. Sheet copper was similarly treated with the same result, except that the blood-red color was tinged with a brownish opalescence, due, no doubt, to the incomplete removal of the nitric acid, since finely divided copper would be more effective in reacting with the acid.

The next question that arose, would other metals have the same effect? To answer this, the following experiments were necessary:

(3) Solutions of ferric nitrate were boiled with an iron nail, reduced iron, iron filings (containing copper), mossy zinc and zinc dust. In each case filtration retained no precipitate on the filter paper. Beautiful red solutions were obtained when the metal was in a finely divided condition and tinged with a brown opalescence when otherwise. Each solution gave

ferric hydroxide when treated with sulfuric acid or the electric current, and obeyed the characteristic tests for colloids. Dialysis gave the crystalloids which were analyzed and found to be, in each case, the nitrate of the metal. In fact the colloids formed by starting directly with ferric nitrate were deeper in color than when nitric acid was employed to first form the nitrate.

The conclusions arrived at are: that hydrolysis was temporarily possible only at the boiling temperature when nitric acid was present in excess; that the addition of a metal combining with the nitric acid formed as a product of the reaction, when the nitrate was used; and with the excess acid when ferric nitrate was formed in the presence of the free acid, favored hydrolysis by destroying the effect of the nitric acid present; that the most favorable condition under which colloidal ferric hydroxide is formed would be one in which the nitric acid was completely removed; and that the finer the state of division of the metal which is used to remove the nitric acid, the deeper red the colloidal solution, since the completeness of the removal of the nitric acid would favor the degree of hydrolysis of the ferric nitrate to colloidal ferric hydroxide.

Experiments are also being carried out to determine whether the nitrates or other salts of the metals would behave similarly, or whether the metals in the electromotive series could be advantageously employed, as was the case with iron and copper salts, to bring about colloidal reactions by precipitating a metal from its solution by one that is more electropositive.

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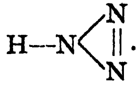
THE REDUCTION OF HYDRONITRIC ACID. II. THE STRUCTURES OF THE TRINITRIDE RADICLE.

BY J W. TURRENTINE.

Received November 12, 1913.

It is the purpose of this paper to show that Fisher's interpretation of the reaction yielding diazobenzeneimide, on which is based the conception of the cycloid structure of the trinitride radicle, is erroneous, since that reaction in all essentials is an oxidation of hydrazine; that in no instance where the oxidation of hydrazine has been studied has a reaction been observed analogous to the one in this case proposed by Fisher. It will be maintained that the interpretation of a reaction which is open to such doubt can not be taken as a sufficient basis for the structure of a compound resulting from this reaction. A new open-chain structure will be proposed for the trinitride radicle and evidence adduced from new reactions observed in a study of the reduction of hydronitric acid and its salts will be brought to bear in support of that structure.

Historical.

Curtius[1] first prepared hydronitric acid from its sodium salt, obtainable from benzoyltrinitride by saponification with sodium hydroxide. Fisher[2] had ascribed the cycloid form to the trinitride group of diazobenzeneimide, previously suggested by Kekulé,[3] from which Curtius logically concluded that the structural formula for free hydronitric acid was  $H—N\langle N=N$.

Fisher prepared diazobenzeneimide, formerly described by Griess,[4] by heating phenylnitroso-hydrazine in a dilute solution of potassium hydroxide. He expressed the reaction by the equation,

$$C_6H_5.N_2H_2.NO = C_6H_5.N_3 + H_2O,$$

and regarded it merely as a splitting-off of water, or a dehydration. Phenylnitroso-hydrazine was prepared from phenylhydrazine hydrochloride by treatment, in cooled solution, with sodium nitrite,[5] as indicated by the equation:

$$C_6H_5.N_2H_3.HCl + NaNO_2 = C_6H_5.N_2H_2.NO + NaCl + H_2O.$$

In hot solution, or in acid solution, the reaction would have gone directly to diazobenzeneimide.[6] Phenylnitrosohydrazine, therefore, can be regarded as an intermediate oxidation product of phenylhydrazine to diazobenzeneimide, or of hydrazine to hydronitric acid. Concentrated sulfuric acid and a few related reagents are capable of extracting the water-forming elements from compounds, but dilute caustic potash can scarcely be so regarded. On the contrary, it is rather a hydrolyzing or saponifying agent. The reaction, then, could not have been a splitting-off of water, but since water was a product of the reaction through the combination of oxygen and hydrogen, it was an oxidation (or reduction).

Superficially, it would appear that the oxidation was intramolecular. It probably is of little moment whether the reaction was intramolecular or resulted from the interaction of the saponification or hydrolysis products of phenylnitrosohydrazine. The reaction, it is maintained, is an oxidation of an organic derivative of hydrazine; and it will be shown in the following paragraphs that the oxidation of hydrazine, or its derivative, yields ammonia, or its derivative, as an additional oxidation product wherever hydronitric acid or its derivative has been produced by that oxidation. There is no reason to suppose that this reaction is an exception.

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[1] *Ber.*, 23, 3023.

[2] *Ann. Chem.* (*Liebig*), 190, 67.

[3] *Lehrbuch*, 3, 230.

[4] *Ann.* (*Liebig*), 137, 65.

[5] Fisher, *Loc. cit.*

[6] Altschult, *J. prakt. Chem.*, [2] 54, 496.

The Oxidation of Hydrazine.

Inorganic.—Due to the researches of Browne and Shetterly on the oxidation of hydrazine[1] it now has become possible to classify the reactions between hydrazine and the oxidizing agents containing no oxynitrogen radicle into three groups: (1) those yielding fairly large amounts of hydronitric acid and ammonia; (2) those yielding little or no hydronitric acid, but large amounts of ammonia, and (3) those yielding little or no hydronitric acid and ammonia.[2] The main point brought out in this investigation, having a bearing on the present discussion, is that, in every instance where hydronitric acid was a product of the oxidation of hydrazine, ammonia also was evolved. This work, as well as that of certain others, also emphasizes the fact that when hydrazine is oxidized by this class of oxidizing agents there is a strong tendency for ammonia to be formed. In fact, in every instance where the oxidation of hydrazine is not complete, that is, does not go completely to nitrogen and water, ammonia is a product of the reaction.

In the work of Browne and Shetterly, ammonia was looked for among the products of the oxidation by 24 oxidizing agents, and in 23 instances it was found to be present. In the 24th case, the oxidation by mercuric chloride, ammonia could not be identified positively. In one other case, that of the oxidation by cupric sulfate, ammonia was present only in traces.

The oxidation of hydrazine by oxidizing agents containing the oxynitrogen group, or a group made up of nitrogen united to negative elements, does not lend itself to such a satisfactory classification. This, probably, in the main, is due to the lack of systematic study of the reactions involved. From an examination of the literature of the subject it becomes evident that in some cases the same reacting substances have given entirely different and even contradictory results in the hands of the different investigators.

Angeli[3] obtained a precipitate of silver trinitride when he allowed silver nitrite, in cold saturated solution, to react with a saturated hydrazine sulfate solution. He proposed the following equation to represent the reaction:

$$H_2N.NH_2 + NO_2H = H_2NN : NOH(+ H_2O) = N_3H + H_2O.$$

Ammonia appears not to have been looked for among the reaction products. Dennsted and Göhlich[4] prepared hydronitric acid from hydrazine sulfate and potassium nitrite in sulfuric acid solution. The presence of ammonia was not noted among the products of the oxidation. The resulting reaction is expressed as follows:

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[1] This Journal, 29, 1305 (1907); 30, 53 (1908); 31, 221 (1909); 31, 783 (1909).

[2] *Ibid.*, 31, 783 (1909); cf. p. 793.

[3] *Ber.*, 26, 885 (1893); *Atti accad. d. Lincei Roma,* [5] 2, I, 569; *Chem. Centr.*, 1893, II, 559.

[4] *Chem. Ztg.*, 21, 876; *Chem. Centr.*, 1897, II, 1073.

$$3N_2H_4.H_2SO_4 + 6KNO_2 + 3H_2SO_4 = 3N_3H + 8H_2O + 6KHSO_4 + 2O + 2N_2O.$$

Tanatar[1] oxidized hydrazine with nitrogen trichloride in alkaline solution. A gas, supposedly nitrogen, was evolved. The presence or absence of ammonia was not mentioned. De Girard and de Saporta[2] employed hydrazine in the determination of copper sulfate and sodium nitrite. The following equation is given to represent the reaction taking place between hydrazine and sodium nitrite:

$$N_2H_4.H_2SO_4 + 2NaNO_2 = N_2 + Na_2SO_4 + 2NOH.$$

It is not stated that ammonia was looked for. In striking contrast with this equation is that proposed by Dennsted and Göhlich, above. In both instances the reaction was carried out in acid solution, hydrazine sulfate, as is well known, gives an acid reaction. Francke[3] records the formation of ammonia as the result of the oxidation of hydrazine by nitrous acid, and has determined the following equation to be a quantitative expression of that reaction:

$$N_2H_4 + HNO_2 = N_2O + NH_3 + H_2O.$$

This equation again is in striking contrast with those proposed by Dennsted and Göhlich and by de Girard and de Saporta. M. J. Brown[4] corroborates Francke's observation relative to the formation of ammonia from the action of nitrous acid on hydrazine (potassium nitrite in sulfuric acid solution), but notes also that hydronitric acid is produced. Thus, practically the same reacting substances, under approximately similar conditions, have yielded four dissimilar sets of results in the hands of as many different experimenters. Thiele[5] observed the formation of hydronitric acid as the result of the action of a nitrite on hydrazine in alkaline solution. No reference is made in the account of the experiment to the simultaneous production of ammonia.

In every case where it is definitely known that ammonia was looked for among the products resulting from the oxidation of hydrazine by the class of oxidizing agents under discussion, ammonia was found. In the one case where ammonia was looked for as an additional oxidation product to hydronitric acid, ammonia was found. This fact appears significant. In the instances cited, ammonia, if not looked for particularly, would have escaped the notice of the investigator. Only a negative result to a definite test can be taken to mean its absence. However, it is scarcely

[1] *Ber.*, 32 1399 (1899).

[2] *Chem. Centr.*, 1904, II, 731.

[3] *Ber.*, 38, 4102 (1905).

[4] THIS JOURNAL, 31, 792 (1909); cf. footnote 6.

[5] *Ber.*, 41, 2681 (1908).

justifiable, in the absence of such tests, to assume the formation of ammonia in every case, however grateful to the argument such an assumption would be, or however strongly such an assumption might appear to be warranted.

The oxidation of hydrazine by that class of oxidizing agents containing no nitro-group is susceptible of such precise classification, and the reactions resulting readily fall into such distinct types, that one is surprised that an analogous classification is not possible with the oxidizing agents containing the nitro-group. It is strongly indicated that a full understanding of the chemistry involved would make possible such a classification, and it is believed that the reaction recorded by M. J. Brown would be typical of a group instead of an isolated instance as it now stands. Still, other results, at variance with that of Brown might ensue through secondary reactions involving the two products of the oxidation, NH_3 and HN_3, causing the elimination of one or the other. On the other hand, it must be admitted that a simultaneous oxidation by the oxygen and nitridation by the nitrogen of the oxy-nitrogen group might induce an entirely different order of reaction, one that is in no wise analogous that by the non-nitrogenous oxidizing agents.

Organic.—In the oxidation of organic hydrazines a similar tendency to form ammonia, or organic derivatives of ammonia, is exhibited. The analogy of the reactions of hydrazine with those of the organic derivatives of hydrazine with oxidizing agents has been pointed out by Browne and Shetterly.[1] Fisher[2] obtained benzene and aniline as the products of the oxidation of phenyl hydrazine by Fehling's solution. Curtius[3] has reviewed a number of reactions involving the oxidation of hydrazine, in all of which ammonia and hydronitric acid, in the form of their derivatives, are formed. Chattaway and Aldridge,[4] in the intramolecular oxidation (reduction) of organic hydrazines, found that (*a*) a primary hydrazine yielded a primary amine, nitrogen and ammonia; (*b*) an unsymmetrical secondary hydrazine yielded a secondary amine, nitrogen and ammonia, and (*c*) a symmetrical secondary hydrazine yielded a primary amine and an azo-compound. In the case of each of the six hydrazines of the various types studied, ammonia or a derivative was an invariable product of the oxidation.

Since the work of Chattaway and others has shown that invariably the intramolecular oxidation of organic hydrazine derivatives results in the formation of ammonia or its derivatives, it is indeed anomalous that ammonia was not a product—if it was not—of the reaction recorded by Fisher. To regard the reaction, as one must, as an oxidation of hydrazine, whether ammonia was formed or not, precludes the acceptance of Fisher's proof of the structure of diazobenzeneimide. To establish the formation of ammonia or a derivative in this reaction, would absolutely falsify this proof.

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[1] THIS JOURNAL, 31, 783 (1909); cf. p. 799.

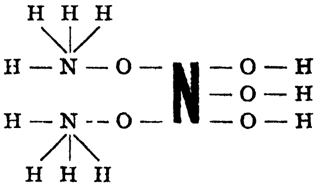
[2] *Ann.*, 190, 67 (1878).

[3] *Ber.*, 26, 1263 (1893).

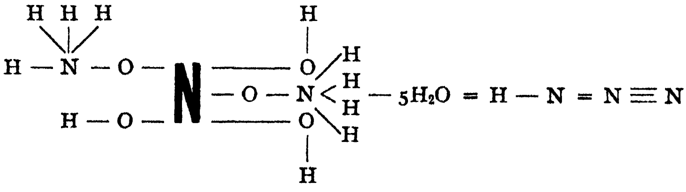
[4] *J. Chem. Soc.*, 99, 100, 404.

The Derivation of the Chain Structure from Certain Theoretical Considerations.

Mendeléeff[1] regarded hydronitric acid as theoretically obtainable from the secondary ammonium ortho-nitrate by the abstraction of five molecules of water. Erdmann[2] prepared orthonitric acid and determined its composition as $N(OH)_5$ or $N_2O_5.5H_2O$. The secondary ammonium salt would be $(NH_4)_2H_3NO_5$. Regarding the oxygen atoms of the orthonitric acid as united to hydrogen to form hydroxyl groups, the structure of the secondary ammonium salt could be represented thus:



In subtracting five molecules of water it should be true that the hydrogen atoms united to oxygen to form hydroxyl would remain so united and would go to make up a corresponding number of molecules of water. On the removal of water, then, there would remain the nuclear pentavalent nitrogen united to the nitrogen of the two ammonia groups, to one of which is attached the only remaining hydrogen atom, one which originally composed a part of an ammonia group. This hydrogen, with the nitrogen to which it is attached, forms an imide group. The result of this dehydration would have to be represented thus:



giving hydronitric acid a chain structure.

Mendeléeff[3] advanced the suggestion that one of the nitrogen atoms of hydronitric acid should be pentavalent and, in attempting to conform to the cycloid conception held by Curtius,[4] proposed the structure,

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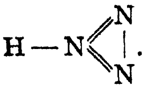
[1] "Principles of Chemistry," second edition, 1, 267.

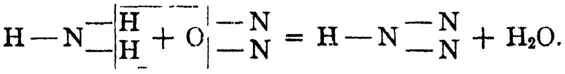
[2] *Z. anorg. Chem.*, 32, 431 (1902).

[3] "Principles of Chemistry," first Eng. Ed., 2, appen. 3, 460; cf. footnote 3, p. 27.

[4] *Ber.*, 23, 3023.

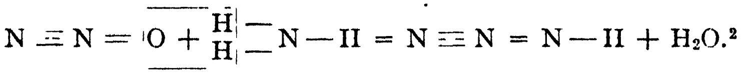


. Preferring to ascribe the simplest possible valence to nitrogen, however, he suggested as more probable the structure, $H{-}N\begin{smallmatrix}-N\\-N\end{smallmatrix}$. As a further argument in favor of this formula he cited the formation of the acid from nitrous oxide, whose structure he regarded as $O\begin{smallmatrix}-N\\-N\end{smallmatrix}$, and ammonia:



$$H{-}N\begin{smallmatrix}-\\-\end{smallmatrix}\left|\begin{smallmatrix}H\\H\end{smallmatrix} + O\right|\begin{smallmatrix}-N\\-N\end{smallmatrix} = H{-}N\begin{smallmatrix}-N\\-N\end{smallmatrix} + H_2O.$$

If nitrous oxide is derivable, however, from primary ammonium orthonitrate, as believed by Mendeléeff, its structure must be $N \equiv N = O$. This conclusion inevitably must be reached if the line of reasoning is followed which is suggested in the analogous derivation of the structure of hydronitric acid from the secondary ammonium orthonitrate. The formation of hydronitric acid from nitrous oxide and ammonia, or more strictly, the formation of sodium trinitride from nitrous oxide and sodium amide, is the basis of the Wislicenus method of preparing hydronitric[1] acid. The structure indicated by the interaction of these substances, therefore, is of special interest as also indicating the open chain structure:



$$N \equiv N = \left|O + \begin{smallmatrix}H\\H\end{smallmatrix}\right|\begin{smallmatrix}-\\-\end{smallmatrix}N{-}H = N \equiv N = N{-}H + H_2O.^{2}$$

Of interest in this connection is the discussion of the structure of trimethylene, ethylene and hydronitric acid by Armstrong, who first questioned the validity of Curtius's formula.[3] Armstrong[4] considered the determination of the structure of nitrous oxide[5] of special importance, "as it is one of a group of compounds including trimethylene, ethylene and diazoimide, all of which it is the fashion at the present moment to formulate as cycloids:

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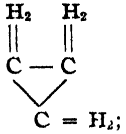
[1] *Ber.*, **25**, 2084; cf. also Dennis and Browne, This Journal, **26**, 577 (1904).

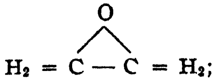
[2] In "designing" structures for compounds, one's ideas are apt to be formed from what one is able to produce on paper rather than by what, from deduction, one knows must be the conditions and relations existing within the molecule. In working out the structures supposedly resulting from the hypothetical reactions, for example, of Mendeléeff, one finds one's self attempting to draw structures wherein the oxygen atoms may be made to appear in juxtaposition to the hydrogen atoms, and, being carried away by this success, is apt to forget that chemical reactions probably take place in more than one plane.

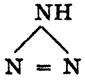
[3] Cf. also Angeli, *Real. Accad. dei Lincei*, **16**, II, 790 (1907), **20**, I, 623 (1911).

[4] *Chem. News*, **67**, 153 (1893).

[5] Gladstone (*J. Chem. Soc.*, **45**, 241) regarded the value obtained by Liveing and Dewar for the molecular refraction of nitrous oxide as favoring the view that nitrogen in that compound has the low value which it exhibits in nitriles.

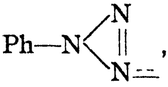




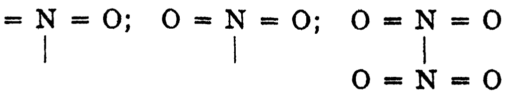


But apparently these is no valid evidence to justify the practice and it is in no way necessary to adopt such a practice."

Quoting further: "Passing now to nitriles and nitrous oxide, we have the most indefinite ideas as to the former: they are conventionally regarded as compounds of triad nitrogen, but this practice is but the outcome of formal obedience to certain artificial, dogmatic rules of valence, and has no real justification. As we must admit the existence of latent affinities in CO, which may be written $-C-O$, we may also admit the possibility of their existence in nitrogen and may represent the nitriles as compounds of the form: $X - \underset{\|}{C} - - N -$. Nitrous oxide on this assumption would be $\equiv N - O - N \equiv$. Diazoimide in like manner, might be regarded as $\equiv N - \underset{|}{N} - N \equiv$, a formula which is implied in Mendeléeff's assumption that it is dinitrile."

The refractive power of the phenyl derivative of diazoimide was determined by Dr. Perkin, the results of which examination did not indicate that diazophenimide was a dinitrile, "nor is it possible to deduce from them any special argument in favor of the formula, , the problem, in fact, remains unsolved."[1]

Much evidence is at hand favorable to Armstrong's idea of the latent valence of nitrogen. Nitrogen in ammonia, for example, is commonly regarded as trivalent, yet it shows a marked tendency to become pentavalent, without displaying any evidence of an oxidation. In fact, it may be made to change back and forth from the trivalent to the pentavalent form without an oxidation or a reduction. The same is true of both of the nitrogen atoms of hydrazine. That of nitric oxide, likewise, unites with oxygen to form the peroxide, which immediately polymerizes to a double molecule, in which the nitrogen atoms must be represented as pentavalent, as:



$$=\underset{|}{N}=O; \quad O=\underset{|}{N}=O; \quad \begin{matrix} O=N=O \\ | \\ O=N=O \end{matrix}$$

Kanonikoff[2] determined the refractivity of the NO_2 group through measurements applied to picric acid; making allowances for the high dispersive power of the latter, he concluded that the nitrogen in this group was pentatomic, with each of the oxygens united to it by a double bond.

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[1] Armstrong, *Loc. cit.*

[2] *J. Russ. Phys. Chem. Soc.*, 1883, 434.

It would be of distinct interest to see if the nitrogens in the trinitride group have the value characteristic of the nitrogen in nitric acid (5.1), or the lower value (4.1) of that in the cyanide group. The value for the trinitride group as now regarded, $-N = N \equiv N$, should be $(2 \times 4.1) + 5.1 = 13.3$; or, the first nitrogen, not occupying the terminal position, might have a still different value.

Before the discussion of the latent valences of nitrogen is concluded, it should be pointed out that nitrogen compounds enter into reactions of two distinct types, both of which involve a seeming change in valence. These are typified by the reaction of ammonia with water, or hydrochloric acid, a reversible reaction, and that of nitric acid on hydrazine, the latter a true oxidation (and reduction), and irreversible.

Experimental.

In a study of the electrochemistry of hydronitric acid and its salts,[1] certain anode reactions were observed which were explainable only on the basis of the supposition that hydronitric acid, or the trinitride ion, was acting as an oxidizing agent. Excessive anode efficiencies were obtained simultaneously with an anodic evolution of nitrogen. Ammonia and, in one case, hydrazine were found to be present in the solution which had undergone electrolysis. When certain reactions, which were supposed to be analogous to those hypothesized as taking place at the anode in trinitride solution, were induced chemically,[2] it was observed that hydronitric acid was an active oxidizing agent. Cuprous oxide in its presence became cupric trinitride, and formed ammonia and free nitrogen as the reduction products of the acid radicle. Metallic copper[3] reacted with the acid to become cupric trinitride, with the production of ammonia and free nitrogen.

The further study[4] of the free acid as an oxidizing agent established the fact that numerous metals lying below magnesium in the electrochemical series dissolved in a dilute aqueous solution of this acid with an evolution of nitrogen and gave rise to the formation of ammonia or of ammonia and hydrazine. This action is of especial importance in view of the fact that the literature dealing with the reactions of hydronitric acid

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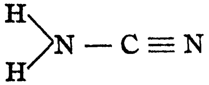
[1] Turrentine, THIS JOURNAL, 33, 803 (1911).

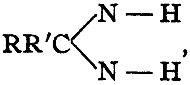
[2] Turrentine and Moore, "The Reduction of Hydronitric Acid by Cuprous Oxide," THIS JOURNAL, 34, 375 (1912). In this connection see "The Action of Hydronitric Acid on Cuprous Chloride and Metallic Copper," *Ibid.*, p. 382.

[3] Turrentine and Moore, *Loc. cit.*

[4] Turrentine, "The Reduction of Hydronitric Acid. I. A Preliminary Note on the Structure of Hydronitric Acid," THIS JOURNAL, 34, 385 (1912).

$H—O—C\equiv N$ Cyanic acid
$H—N=C=O$ Isocyanic acid[1]
$H—S—C\equiv N$ Thiocyanic acid
$H—N=C=S$[2] Isothiocyanic acid

$H_2N—C\equiv N$ Cyanamidic acid
$H—N=N\equiv N$ Hydronitric acid

Assuming the correctness of the structures here given, it is seen that oxygen may occupy any of the three positions and in ozonic acid occupies all three at the same time. Sulfur is found in the α-position in thiocyanic acid and in the γ-position in the isothiocyanic acid. Carbon shows less mobility. Nitrogen, finally, is found in the α-position in isothiocyanic acid in the γ-position in cyanic acid and in the β-position in the fulminates. In cyanamides, it occurs simultaneously in both the α- and the γ-positions. In hydronitric acid it appears simultaneously in all three positions.

Since the announcement by the writer of his conception of the chain structure of the trinitride radicle, but before its publication in the form of a journal article,[3] Thiele[4] announced his derivation of the same structure. Thiele's deductions were based on certain experiments which showed that the condensation products of hydrazine with ketones, instead of being hydrazi-compounds,  $RR'C\langle{}^{N-H}_{N-H}$, are in fact hydrazones, $RR'C=N—N=H_2$. The oxidation of the latter leads to the formation of diazo-compounds with such ease as to justify the conclusion that the hydrazones contain an open chain rather than a ring structure. Other arguments are advanced by this author, all of which are attacked by Forster,[5] who fails, however, to bring ,to his assistance any experimental evidence whatever and bases his arguments entirely on what appear as probabilities.

Franklin, in his interesting work on the ammonia system of acids, bases and salts,[6] frequently has referred to the amides of the respective acids as ammono-acids and has shown that the amides in their relation to ammonia are strictly analogous to the acids in their relation to water. In its bearing on the matter under discussion in the present paper, the following quotation from Franklin[1] is of especial interest:

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[1] The position of the nitrogen in cyanic and isocyanic acids appears to be in some doubt.

[2] The structure assigned to mustard oils.

[3] Turrentine, *Loc. cit.*

[4] *Ber.*, 44, 2522 (1911).

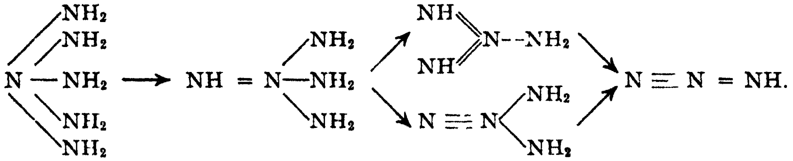
[5] "Structure of the Azoimide Nucleus," *Trans. 8th Intern. Congr. Appl. Chem.*, 6, 108 (1912).

[6] *Am. Chem. J.*, 21, 8 (1899).

"More perfect analogs of the aquo acids, however, would be compounds entirely devoid of oxygen, and in which all the functions of oxygen in the aquo acids are performed by nitrogen.

"If, after the familiar manner, acetic acid, carbonic acid, and nitric acid, and their anhydrides are assumed to be derived from the normal acids of the respective formulas, $CH_3C(OH)_3$, $C(OH)_4$, and $N(OH)_5$ by successive dehydration, the formulas for strictly analogous ammono acids and their anammonides may be deduced from the hypothetical ammono acids of the formulas, $CH_3C(NH_2)_3$, $C(NH_2)_4$ and $N(NH_2)_5$.*****

"Normal ammono nitric acid and its deammonation products [are then represented] by the formulas



"The indicated successive deammonation of nitrogen pentamide is especially interesting in view of the fact that the formula of the final product is identical with that recently proposed********for hydronitric acid. The experimental work*****shows very clearly the analogy between hydronitric acid and nitric acid as acids, respectively, of the ammonia and water systems, and proves to a practical certainty the correctness of the formula $HN = N \equiv N$ for hydronitric acid."

[Contribution from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 97.]

ON THE RELATION BETWEEN THE CONDUCTANCE AND THE VISCOSITY OF ELECTROLYTIC SOLUTIONS AND ITS BEARING ON THE THEORY OF THESE SOLUTIONS.

By Charles A. Kraus.

Received October 11, 1913.

1. Introduction.[2]

That the conductance of an electrolytic solution is dependent on its viscosity was first suggested by G. Wiedemann(1)[3] in 1856. The experiments on which Wiedemann based his conclusions are not decisive in the light of our present knowledge; nevertheless, he correctly inferred that if the conductance of solutions is a simple function of their viscosity, then the conduction process must consist in a migration of carriers through the solution under the influence of the impressed potential gradient and against the opposing frictional resistance of the surrounding molecules.

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[1] "The Organic Acid Amides and their Metallic Derivatives as Acids and Salts of the Ammonia System of Acids, Bases and Salts," *Trans. 8th Intern. Congr. Appl. Chem.*, 6, 119 (1912).

[2] This investigation was assisted by a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington. I wish to express my indebtedness for this assistance whereby the completion of this work was made possible.

[3] References to earlier papers will be found in the collected list of references at the end of this paper.

Grotian(2) subsequently adduced conclusive evidence connecting the conductance with the viscosity of solutions, by showing that the temperature coefficients of conductance and fluidity are practically identical. Stephan(3) studied the conductance and viscosity of solutions in mixtures of alcohol and water and found that, with increasing dilution, the ratios of the products of conductance and viscosity in these mixtures to that in pure water approach approximately the same limiting value. He also found that for these solutions the temperature coefficients of conductance and fluidity are substantially the same.

The law of the independent motion of the ions was discovered by Kohlrausch(4) as a result of the consideration that in dilute solutions the motion of the ions is entirely controlled by the frictional resistance due to the solvent. He accounted for the increase in conductance with temperature, by assuming a decrease in the frictional resistance due to the solvent as a result of its greater fluidity. Kohlrausch also pointed out the important fact that, with increasing temperature, the difference in the conducting power of different electrolytes diminishes.[1]

Arrhenius(5) finally established the ionic theory of electrolytic conduction on a quantitative basis, and thereafter it was possible to study the relation between conductance and viscosity under widely varying conditions. Ostwald(6), after having shown that the law of mass-action applies to solutions of the weak acids, attempted to harmonize discrepancies arising between the measured and the calculated conductance values of concentrated solutions of butyric acid in water, by correcting the observed conductances in direct proportion to the fluidity change of the solution.

Arrhenius(7) made an extensive investigation of the influence of various non-electrolytes on the conductance of electrolytic solutions in water. He found that, for a given percentage addition of various non-electrolytes to solutions of a given electrolyte, the conductance change varies, being greater for substances of high molecular weight. For a given non-electrolyte, the conductance change was found to vary with the nature of the dissolved electrolyte, being in most cases greater for electrolytes with slow ions. From the results of Arrhenius it appears that, for a given viscosity change, the change in conductance is greater the smaller the dimensions of the molecules of the added non-electrolyte, and the greater the dimensions of the ions of the dissolved electrolyte. Arrhenius recognized the fact that different ions experience different changes in the resistance to their motion as a result of viscosity change, and he suggested that the observed change in the transference numbers of various electrolytes with concentration is due to the specific influence of the accompanying viscosity change on the speed of the anion and the cation, respectively.

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[1] Kohlrausch(4) p. 196.

In recent years many investigations have been carried out on the relation between the conductance and the viscosity of solutions. Walden(8) has pointed out that for a given electrolyte in various solvents the Λ_0 values are very nearly proportional to the fluidities of these solvents. Martin and Masson(9), Jones and his associates(10), Fawsitt(11), Hartley, Thomas and Appleby(12), Green(13), and others have studied the relation between the conductance of electrolytic solutions containing nonelectrolytes and the viscosity of these solutions. Bousfield(14), R. Lorenz(15), Herzog(16), and others have attempted to apply to solutions of electrolytes the laws which have been found to hold between the dimensions and the mobilities of colloidal particles in solution.

Johnston(17) investigated the relation between the conductance and fluidity of dilute aqueous solutions at temperatures as high as 156°, employing the conductance data obtained by Noyes(18) and his associates in this laboratory. Johnston found that this relation may be expressed by the equation:

$$\Lambda_o = kf^p. \qquad \text{(I)}$$

When k and p are constants, Λ_o is the limiting conductance of a given electrolyte at any temperature and f is the fluidity of water at the same temperature. Johnston showed that p does not differ greatly from unity,[1] generally being less, and that it has a specific value for the individual ions. Recently, Washburn(19) has proposed to apply a correction for viscosity to the conductance of each ion, assuming that the change in speed which an ion experiences, as a result of a given viscosity change with concentration, is the same as that which it experiences for the same viscosity change due to temperature change. In other words, in making corrections for the viscosity effect due to concentration change, he employs the exponent p of Equation I, determined by Johnston from temperature change. How far this assumption is justified will appear below.

2. General Considerations.

It is the purpose of this paper to investigate the conditions under which corrections may be applied to conductance values for the influence of viscosity and to interpret the results in the light of the ionic theory, but, before examining the experimental data, it will be well to inquire into the principles underlying viscosity change in order that the data may be correctly interpreted. The slipping of the particles of a fluid with respect to one another or the motion of a particle through a collection of other particles is peculiarly dependent on the relative dimensions of the various particles concerned. This is shown by the work of Millikan(20) who investigated the motion of small charged particles of oil through air. If the moving particles are small with respect to those of the surrounding medium, their speed will undoubtedly be greater than would be that of larger particles in the same medium.

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[1] With the exception of the case of the hydrogen and hydroxyl ions.

It is evident that, in interpreting the influence of viscosity on conductance, the relative dimensions of the ions and of the various molecules which resist the motion of the ions, are of primary importance.

Change in viscosity is, in general, brought about in one of three ways, namely: first, change in concentration, which may be due either to the addition of a new substance or of a larger amount of one already present in solution; second, change in pressure; and, third, change in temperature.

The influence of the viscosity change on the speed of an ion in a solution will, in general, differ with the nature of the process by means of which the viscosity change is brought about. I shall consider below, and in order, the relation between the change of ionic speed and the change of viscosity as it is brought about in the different ways suggested above.

3. Experimental Material.

A. *Viscosity Change Produced by Concentration Change.*

In many respects the most important case to be considered is that in which the viscosity change is due to the electrolyte itself, the speed of whose ions are under consideration; for this case arises whenever the concentration of a solution approaches normal, and in many cases at much smaller concentrations. If we are to determine the concentration of the ions at higher concentrations by the conductance method, it is essential that the law be known connecting the speed of the ions with the concentration of the solution. It is not obvious that the viscosity factor is the only one influencing the speed of the ions as the concentration increases. I shall, however, show below that this is the case in some instances.

The greatest difficulty which it has been necessary to overcome, in attacking this problem, has been the lack of a law connecting the conductance and concentration of solutions. As is well known, the law of mass action does not apply, even approximately, to solutions of strong electrolytes in water. Other relations than the mass-action law have been suggested, notably the law of Storch(22) which may be expressed by the following equation:

$$(c\gamma)^n/c(1 - \gamma) = D. \qquad \text{(II)}$$

Where n and D are constants, c is the concentration and γ is the degree of ionization. γ is determined by the equation:

$$\gamma = \Lambda/\Lambda_0. \qquad \text{(III)}$$

where Λ is the conductance at concentration c, and Λ_0 is the equivalent conductance which is approached as the concentration of the solution approaches zero. It is obvious that, if the speed of the ions changes, the value of Λ_0 for each ion must be corrected proportionately.

It has been found that the law of Storch does not apply strictly in dilute solutions, where the viscosity effect is negligible, and, therefore, any extrapolation to more concentrated regions is rendered uncertain. It has recently been shown by Kraus and Bray(23)[1] that, for a large number of electrolytes in various solvents, the following equation holds:

$$(c\gamma)^2/c(1 - \gamma) = D(c\gamma)^m + K, \qquad \text{(IV)}$$

where m and K are constants and the other symbols possess the same significance as above. At high concentrations K becomes negligible in comparison with $D(c\gamma)^m$ and the equation reduces to the form of Equation II. The wide range of applicability of this equation justifies its application as an extrapolation function to more concentrated solutions. The influence of viscosity may then be determined by comparison with the extrapolated values from this equation.

Any arbitrariness in this procedure may be overcome by studying a system in which the solution possesses a minimum viscosity. In such solutions the viscosity at first decreases with concentration, then increases again, and finally becomes greater than that of the pure solvent. The point at which the viscosity of the solution becomes equal to the viscosity of the solvent thus furnishes a reference point, by means of which the validity of the extrapolation may be checked without any arbitrary assumptions.[2]

By way of illustration, the results of such a calculation are given for potassium iodide dissolved in water at 0°, in which case the viscosity change is very large. The conductance data in concentrated solutions are due to Sloan(24). Those in dilute solution are due to Kahlenberg(25).

The last five of Kahlenberg's values in dilute solutions were employed in determining the value of Λ_0 for KI. These last five points agree with the data of Sloan. They do not, however, agree with the remainder of Kahlenberg's determinations, which appear to be uniformly low. The value of Λ_0 obtained, and employed throughout these calculations, is 81.12. This value is in good agreement with the Λ_0 value employed by Washburn and MacInness(26) for KCl, which is 81.0. A small error in Λ_0 will not affect the extrapolation function in concentrated solutions to a marked degree. The experimental data are shown graphically in Fig. 1, where values of Λ are plotted as ordinates and those of log c as abscissas. Sloan's determinations are represented by circles and Kahlenberg's by crosses. It will be observed that in concentrated solutions the conductance curve exhibits a distinct minimum and maximum. As we shall see below, this peculiar trend of the curve is due to viscosity change.[1]

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[1] See also Kraus and Bray(49).

[2] This condition is partially fulfilled in the case of solutions of KI in water.

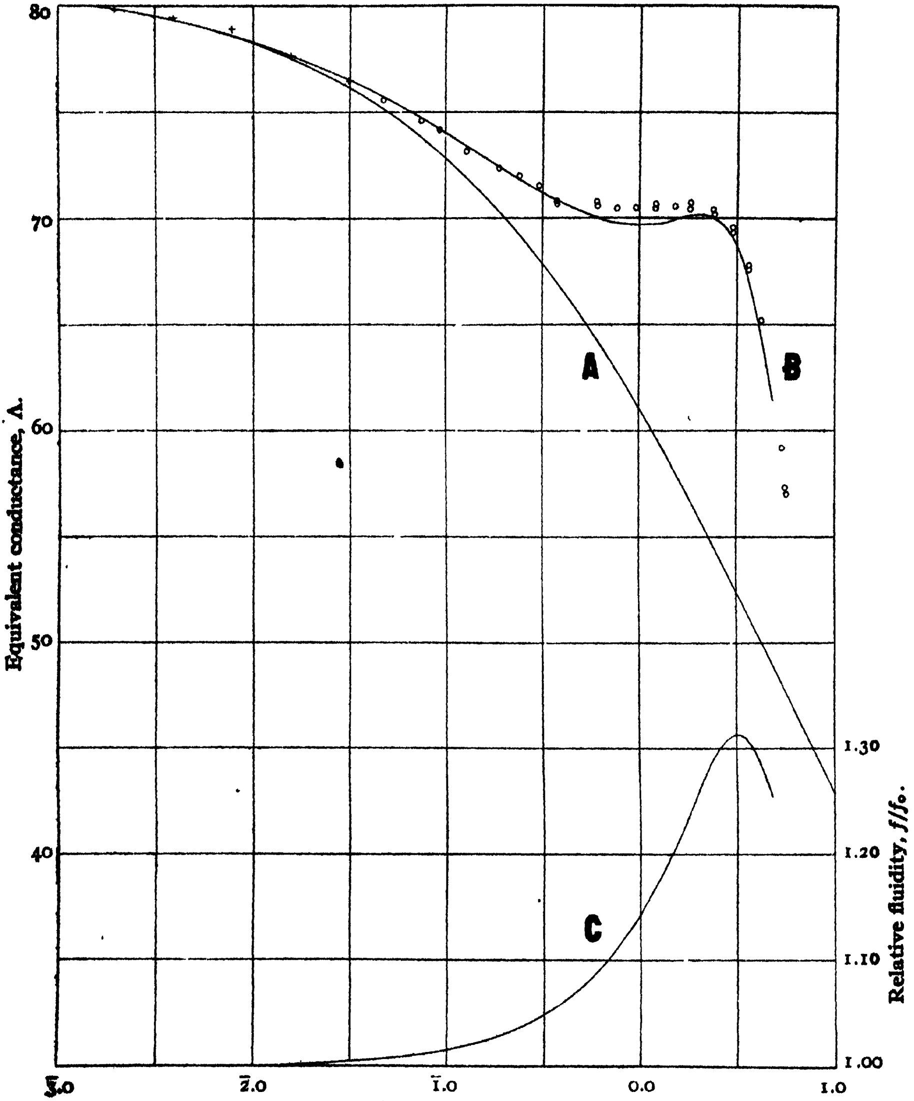

Fig. 1.—Fluidity and conductance curves for KI in water at 0°.

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[1] Washburn(42, p. 1464) has suggested that the maxima and minima frequently observed in the conductance curves of solutions, are due to viscosity change. In the case of non-aqueous solutions, in which this phenomenon occurs most frequently, the minimum is not due to viscosity change, as has been shown by Kraus and Bray (49). Only in the case of aqueous solutions are both the maximum and minimum due to viscosity.

The viscosity data are due to Sprung(27). The fluidity curve of potassium iodide at 0° is represented graphically in Fig. 1 (Curve C), values of f/f_0 being plotted as ordinates, f_0 being the fluidity at zero concentration and f the fluidity at concentration c. The lowest temperature at which Sprung measured the viscosity of KI was 5°. The values at 0° were obtained by graphical extrapolation. In Table I the concentration c of the solution is given in the first column; Λ, the conductance, as determined by Sloan and Kahlenberg, is given in the second column; and in the third column are given the values of n, the viscosity, as obtained by extrapolation.

TABLE I.—CONDUCTANCE AND VISCOSITY DATA FOR POTASSIUM IODIDE IN WATER AT 0°

C.	Λ.	η.
5.662	57.30	0.8330
5.420	59.17	0.8145
4.818	64.33	0.795
4.218	65.20	0.777
3.623	67.83	0.765
3.614	67.65	0.765
3.012	69.31	0.763
2.410	70.40	0.777
1.807	70.40	0.809
1.506	70.43	0.831
1.205	70.61	0.856
0.7528	70.46	0.900
0.6025	70.65	0.9185
0.3772	70.83	0.946
0.3012	71.56	0.9565
0.2410	72.03	0.965
0.1884	72.36	0.9725
0.1280	73.13	0.981
0.09417	74.13	0.986
0.07528	74.55	0.989
0.04706	75.60	0.9927
0.03125	76.5	0.995
0.01563	77.7	0.9975
0.007812	78.9	0.9987
0.003907	79.4	. .
0.001953	79.8	.

Since the fluidity of the solutions in question is greater than that of pure water, it seemed reasonable to assume that, whatever the mechanism to which the fluidity change may be due, the ions in their motion will not meet with molecules or molecular aggregates that are larger than those in pure water. Accordingly, the several conductance values were corrected in direct proportion to the viscosity change, each value of Λ being multiplied by the corresponding value of the viscosity ratio η/η_0.

These values were then tested by means of the extrapolation Function II which is a special case of the more general Function IV as already explained. Equation II may be written in the form:

$$n \log (c\Lambda) = \log [c(\Lambda_o - \Lambda)] + \log D\Lambda_o^{n-1}, \qquad \text{(V)}$$

which is the equation of a straight line when $\log (c\Lambda)$ and $\log [c(\Lambda_o - \Lambda)]$ are considered as variables.

In Fig. 2 this function is plotted for solutions of potassium iodide in water at 0°, values of $\log (c\Lambda)$ being plotted as abscissae and values of $\log [c(\Lambda_o - \Lambda)]$ as ordinates. The scale, in each case, is indicated on the lower and left hand margins, respectively. The circles represent points in which the conductance has been corrected for viscosity, while the crosses represent the same points without any viscosity correction. The distance between the two series of points gives a fair idea of the extent of the viscosity correction, which at its maximum is a little over 30%.

It is apparent, on inspection, that the circles all lie on a straight line and that the points in the more dilute solutions, where the correction for viscosity is small or negligible, also follow this line. It is thus demonstrated that, in the case of solutions of potassium iodide in water, Equation II, and by consequence also the more general Equation IV, is obeyed up to a concentration as high as 5.66 normal, and that the speed of the ions over this range is a linear function of the fluidity within the limits of experimental error.

In Fig. 1, the continuous curve marked *B*, passing through the experimental points, represents the equation

$$(c\Lambda')^2/c\Lambda_o(\Lambda_o - \Lambda') = D(c\Lambda'/\Lambda_o)^{n-1},$$

where $D = 2.62$, $\Lambda_o = 81.12$, $n = 1.51$, and $\Lambda' = \Lambda\eta/\eta_0$. The branch-curve marked *A* represents the conductance curve of KI on the assumption that no change in speed has taken place. The points on Curve *B* are thus obtained by multiplying the conductance values of Curve *A* by the viscosity factor η/η_0.

The agreement between the experimental and the calculated values is fully as good as the experimental data lead us to expect. The maximum and minimum of the conductance curve are perfectly reproduced in the calculated curve. A comparison with the fluidity curve (*C*), which appears on the same figure, shows clearly how the minimum and maximum result from the peculiar form of the fluidity curve.

The negative viscosity effect in potassium iodide at 0° is the largest for which both conductance and viscosity data are available. The correction has likewise been applied to potassium iodide, ammonium chloride, and potassium chloride at 18°,[1] all of which give solutions having a viscosity smaller than that of water. In all of these cases the agreement with Equation II, after correcting for viscosity in proportion to the viscosity change, is within the limits of experimental error. The viscosity correction in these cases is much smaller than it is in the case of potassium iodide at 0°.

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[1] For KCl see Kraus and Bray(49), p. 1407, *et seq.*

Solutions of salts whose viscosities are greater than that of water have also been investigated. In the case of sodium nitrate, when corrected for viscosity in direct proportion to the viscosity change, the resulting curve agrees with Equation II as well as could be expected, since the data are not very consistent among themselves. In the case of sodium chloride and sodium acetate, the corrected conductance is greater than it should be according to Equation II.

The behavior of salts of this type is well illustrated in the case of lithium chloride at 0°. The viscosity change for this salt is very great. At normal concentration the viscosity of a lithium chloride solution is 12.4% greater than that of water. Up to this concentration the very excellent conductance and viscosity measurements of Washburn and MacInness(26) are available. I have, therefore, selected this salt as a typical example whereby to illustrate the relation between conductance and viscosity where the latter is larger than that of pure water.

In Fig. 2, the upper plot represents the Function V for lithium chloride. Curve *A* represents the function before any correction has been applied for viscosity. Curve *B* represents the function after multiplying the conductance by the viscosity ratio. It is evident that in the first case the deviation from a straight line is due to the influence of viscosity. On the other hand, the pronounced departure of Curve *B* from the experimental points shows that the speed of the ions is affected far less than the viscosity of the solution as a whole. For reasons which I shall elucidate more fully below, I have constructed a third curve, *C*, on the assumption that the speed of the lithium ion varies in direct proportion to the change in the fluidity of the solution, but that the speed of the chlorine ion remains unaltered. As may be seen by inspection, the Function II gives an excellent straight line when the conductances are corrected in this manner.

At higher concentrations than normal, the correction of the conductance of one ion alone will not suffice; although even up to 9 normal the correction factor is always less than corresponds to the viscosity change of the solution. Beyond 9 normal the correction factor again begins to decrease rapidly.[1] In obtaining the results discussed in this paragraph, the conductance and viscosity data of Green were employed. Green's conductance data, in dilute solutions, are not entirely satisfactory, and only a qualitative result can be obtained as to the general trend of the change in conductance with viscosity. There is, however, no question as to its general character.

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[1] This is shown by an increase in the ratio Λ/f, at this point, which is clearly brought out in Fig. 5, page 2045 of Green's paper(13). The increase in Λ/f beyond 9 normal is doubtless due to increasing speed of the ions in consequence of dehydration.

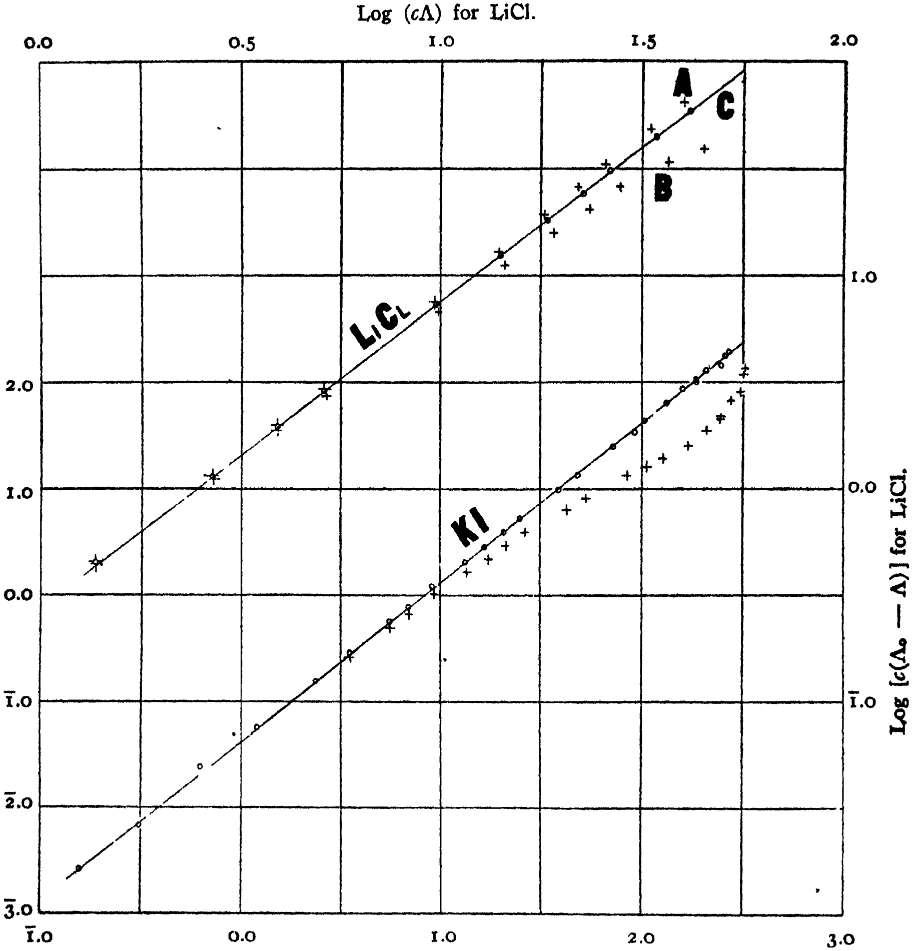

Fig. 2.—Plots for KI and LiCl in water as 0°.

Data relating to the conductance and viscosity of non-aqueous solutions are very meagre. In the case of ammonia solutions, however, the conductance data of Franklin and Kraus(28), and of Franklin(29) and the viscosity measurements of Fitzgerald(30) make it possible to determine the general character of the relationship between conductance and viscosity in the case of this solvent. Kraus and Bray have recently shown that Equation IV holds for ammonia solutions within the limits of experimental error up to concentrations which, in some cases, are above normal. In general, this concentration is higher the smaller the molecular weight of the electrolyte and the greater the speed of its ions. For potassium iodide the equation holds to normal concentration. At higher concentrations, the conductance values calculated from Equation IV are greater than the experimental ones.

This phenomenon appears to be a very general one and is particularly evident in the case of solvents of relatively low dielectric constants, in which case the exponent *m* of Equation IV is greater than unity. When *m* is greater than unity the conductance curve passes through a minimum, usually in the neighborhood of 1.0 to 0.10 normal concentration, to both sides of which the conductance rises. The experimental values, however, after passing through the minimum, reach a maximum in the more concentrated solutions, after which they continue to decrease indefinitely. Franklin and Gibbs(31) and Franklin(32) have suggested that this final drop in the conductance curve, in concentrated solutions, is due to in-

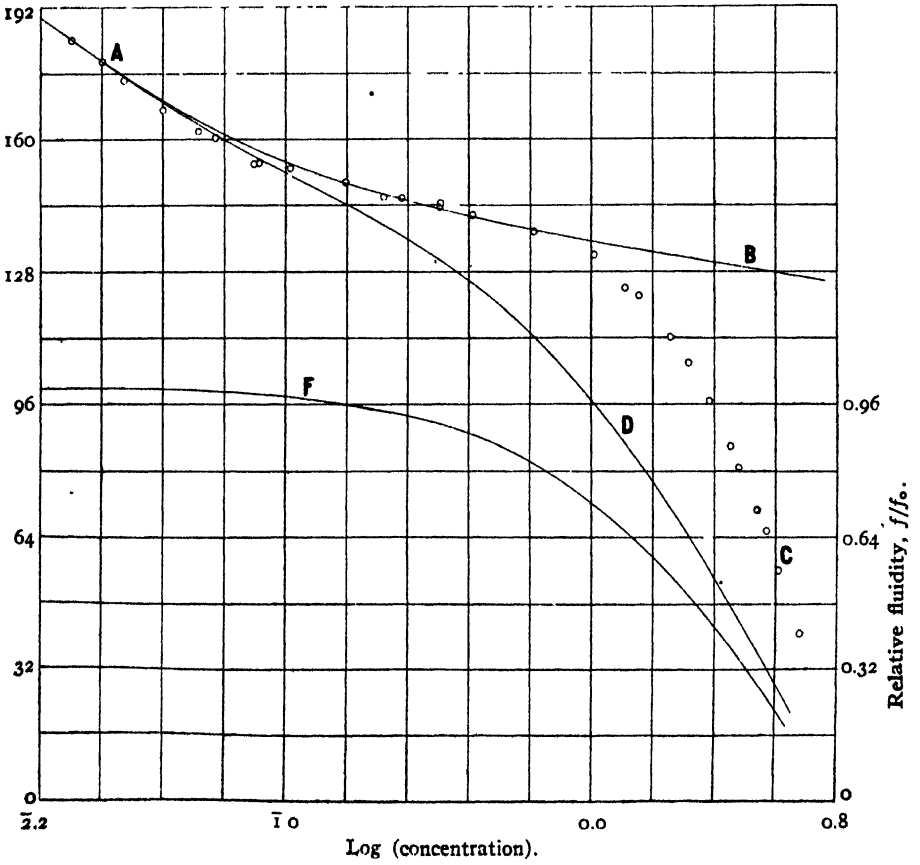

Fig. 3.—Conductance and fluidity curves for KI in NH_3 at —33.5°.

creasing viscosity of the solution. In case m is not greater than unity, the conductance curve does not pass through a minimum and a maximum, but the curve exhibits double curvature, indicating that the same factors are operative in this case as in the one in which m is greater than unity.

In Fig. 3 are shown the conductance and fluidity curves for solutions of potassium iodide in ammonia. Values of log c are plotted as abscissae and values of Λ as ordinates. The scale is indicated on the lower and left hand margins. Curve AB is the conductance curve calculated on the assumption that the mobility of the ions does not change with concentration. Curve AC is the experimental curve, the various points being indicated by circles. Curve AD is the conductance curve, calculated on the assumption that the mobility of the ions is proportional to the fluidity of the solution. The viscosity data are due to Fitzgerald; the fluidity curve (F) is shown in the lower portion of Fig. 3, values of the relative fluidity, f/f_0, being plotted as ordinates and of log c as abscissas. The scale of ordinates is indicated on the right hand margin of the figure, while the scale of abscissae is the same as that of the conductance curves.

B. Change in Viscosity and Conductance Due to Added Non-electrolytes.

When the viscosity change is brought about by the addition of a non-electrolyte, a conductance change takes place in the direction of the viscosity change, but in most cases the conductance change is smaller than the corresponding viscosity change. The experimental material is very incomplete. It is fairly evident, however, that the smaller the molecules of the added non-electrolyte and the larger the ions, the more nearly does the conductance change in direct proportion to the fluidity change.

It has been found that, for small additions of non-electrolytes, the relation between conductance and fluidity may be represented by an equation of the form of Equation I, in which p and k are constants, Λ_0 is the limiting conductance of the electrolyte in the solution containing the non-electrolyte, and f is the fluidity of the solution. The less the conductance of the electrolyte is influenced by the fluidity change, the smaller will be the value of p. Table II, which is reproduced from Green's paper(13), shows the value of p for various solutions.

TABLE II.—CHANGE OF CONDUCTANCE OF ELECTROLYTES DUE TO ADDED NON-ELECTROLYTES.

Electrolyte.	Non-electrolyte.	p.
HCl	Sucrose	0.55
KCl	Sucrose	0.70
LiCl	Sucrose	0.70
$CuSO_4$	Glycerol	1.0
NaOH	Carbamide	1.0
KCl	Carbamide	1.0
$LiNO_3$	Pyridine	1.0–1.3

An inspection of the table shows that, in the case of sucrose, the conductance of hydrochloride acid is affected much less than that of KCl or LiCl. In the case of $CuSO_4$, the conductance change is proportional to the viscosity change due to the added glycerol. The molecular weight of glycerol is much smaller than that of sucrose, while the dimensions of the Cu^{++} and SO_4^{--} ions are doubtless greater than those of the K^+, Cl^-, or H^+ ions. Carbamide, with a molecular weight of only 60, influences the conductance of both NaOH and KCl in direct proportion to the fluidity change.

C. The Influence of Pressure on Viscosity and Conductance.

So far as our present knowledge goes, water is the only solvent whose viscosity decreases with increasing pressure. The viscosity does not, however, continue to decrease indefinitely, but passes through a minimum after which it begins to increase rapidly. The minimum lies in the neighborhood of 1000 atmospheres. At higher temperatures the minimum becomes less and less pronounced and finally disappears altogether. The viscosity-pressure curve bears a striking resemblance to the viscosity-concentration curve of electrolytes which exhibit negative viscosity. Tammann[1] has shown that certain properties of solutions are comparable to the properties of water under pressure. He thus ascribes the influence of salts on the properties of water to the influence of internal pressure. However, we may look at the phenomenon, there can be no doubt that the negative viscosity effects, exhibited by water under pressure and by aqueous solutions under the influence of an added solute, are due to the same kind of molecular changes.

Tammann(33) has investigated the conductance of solutions of strong electrolytes in water under pressure. Some of his results for sodium chloride are reproduced in Fig. 4, where values of the relative resistance, R/R_0, are plotted as ordinates and the pressures in kilograms per square centimeter as abscissae. The continuous curves are drawn to pass through these points. The upper curve represents the results at 20° and the lower those at 0°. The concentration of the sodium chloride solution was 0.1 normal. It is unlikely that the trend of the conductance-pressure curve is materially influenced by change in ionization at this concentration. The circles represent the fluidity of pure water as determined by Cohen(34), the upper points representing the results at 15° and the lower those at 1°, respectively.

It is evident that the conductance curve of the NaCl solution corresponds very closely with the fluidity curve of pure water as determined by Cohen, coinciding within the limits of experimental error. This result is of great importance, since it shows that, while the conductance of a sodium chloride solution is affected far less than the viscosity by concentration change of the electrolyte, the conductance of the same ions is affected in proportion to the fluidity by the pressure change.

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[1] Tammann, *Eigenschaften der Lösungen*, Göttingen, 1906.

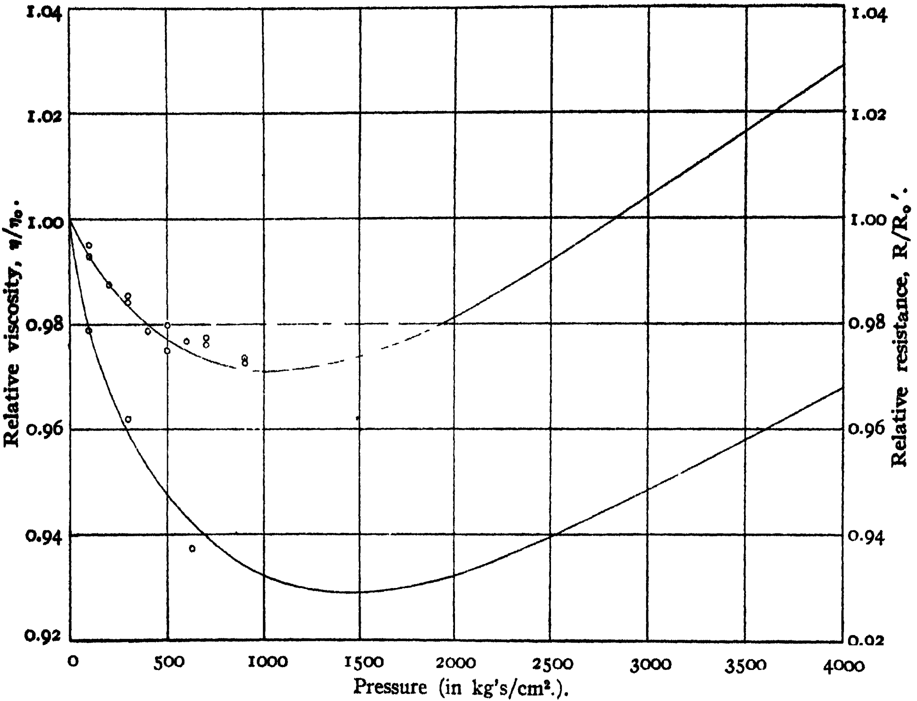

Fig. 4.—Showing the influence of pressure on conductance and viscosity.

The important conclusion may, therefore, be drawn that *viscosity change affects the same ions differently when the viscosity change is brought about by different causes.* We shall inquire into the nature of this phenomenon more particularly after having presented the results of the next section.

D. The Influence of Temperature on Conductance and Viscosity.

As regards the influence of temperature, various electrolytes exhibit great uniformity in their behavior, although differing greatly in degree. Kohlrausch(35) was the first to point out the relation between the ionic conductance and the temperature coefficient of ionic conductance. A paper by Johnston has already been mentioned in which he showed that the Λ_0 values of different ions may be expressed as a simple exponential function (Equation I) of the fluidity[1] of the pure solvent. The following table gives the values of p for univalent and bivalent ions:

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[1] Kohlrausch(47) first showed that the conductances of the ions in water follow the fluidity curve of water at different temperatures, particularly in the case of the larger ions. His conclusions, however, were based on the results for a much smaller temperature interval than Johnston's.

TABLE III.—INFLUENCE OF TEMPERATURE ON ION CONDUCTANCES.

Univalent Ions.

Ion.	Cl^-.	K^+.	NH_4^+.	NO_3^-.	Ag^+	Na^+	$C_2H_3O_2$
p......	0.88	0.887	0.891	0.807	0.949	0.97	1.008
Λ......	65.4	64.7	64.4	61.8	54.0	43.5	34.6

Bivalent Ions.

Ion.	$^1/_2SO_4^{--}$.	$^1/_2C_2O_4^{--}$.	$^1/_2Ba^{++}$	$^1/_2Ca^{++}$
p...............	0.944	0.931	0.986	1.008
Λ....................	68.7	63.8	55.9	52.1

In Table III, the different ions are arranged in order of decreasing conducting power. It will be seen that, in the case of the univalent ions, this order corresponds with the order of increasing values of p, with one exception in the case of the NO_3^- ion. The same relation holds for the bivalent ions with one exception in the case of the $C_2O_4^{--}$ ion (which, however, is probably within the limits of experimental error). It is evident that there is an intimate relation between the conductance of an ion, and the change of its conductance with fluidity change, due to change in temperature.

Only two of the ions have an exponent greater than unity. These are $C_2H_3O_2^-$ and Ca^{++}. Both of these ions have very low conductance values, being, respectively, the final members of the two series. Whether the exponent is actually greater than unity is doubtful; for the Λ_o values under the best conditions are probably not accurate to more than 2%.[1] At higher temperatures the values may be expected to be correspondingly less certain. As the size of an ion increases, it is probable that, ultimately, its speed will become a linear function of the viscosity. That its speed should change more rapidly than viscosity does not seem probable unless the dimensions of the ion change. In order to bring out this relation, and to show that it holds at high temperatures as well as at low, the conductances of the different univalent ions have been compared with that of the $C_2H_3O_2^-$ (acetate) ion. Johnston has shown that this ion changes its speed proportionally to the fluidity of water. The ratios of the conductances of the different ions to that of the $C_2H_3O_2^-$ ion are given in Table IV and are shown graphically in Fig. 5. Under f' are given values of the fluidity divided by the conductance of the $C_2H_3O_2^-$ ion. Since the conductance of this ion is proportional to the fluidity of the solvent, the ratio of f to the conductance of the acetate ion remains constant and independent of temperature. At 306° the conductance of the acetate ion was approximated from that of the sodium ion.

In Fig. 5 the relative conductance of the various ions (with respect to the conductance of the acetate ion) are plotted as ordinates against temperatures as abscissae. On the left hand margin, the various curves

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[1] Compare Kraus and Bray(49), p. 1410, *et seq.*

TABLE IV.—INFLUENCE OF TEMPERATURE ON THE CONDUCTANCE OF VARIOUS IONS RELATIVE TO THAT OF THE ACETATE ION.

Ion.	0.0°.	18°.	25°	50°.	75°.	100°.	128°.	156°.	218°.	306°.
K^+	1.99	1.87	1.83	1.72	1.66	1.58	1.54	1.50	1.32	1.18
Na^+	1.28	1.26	1.25	1.22	1.20	1.19	1.19	1.18	1.15	1.11
NH_4^+	1.98	1.86	1.83	1.72	1.66	1.59	1.55	1.52	1.37	1.30
Ag^+	1.62	1.57	1.54	1.51	1.49	1.45	1.43	1.42	1.29	..
Cl^-	2.02	1.89	1.85	1.73	1.67	1.59	1.54	1.51	1.32	..
NO_3^-	1.99	1.78	1.73	1.55	1.46	1.37	1.30	1.25	1.21	..
H^+	11.82	9.08	8.58	6.95	5.88	4.95	4.23	3.68	2.79	1.82
OH^-	5.17	4.95	4.71	4.24	3.75	3.38	3.07	2.81	2.08	1.62
f'	2.73	2.72	2.73	2.71	2.72	2.71	2.71	2.71	..	..

are marked with the symbols of the ions to which they relate. The curves for potassium, ammonium and chloride ions differ so little that they are represented by a single curve, that of the K^+ ion. The curve for the NO_3^- ion is indicated by a broken line.

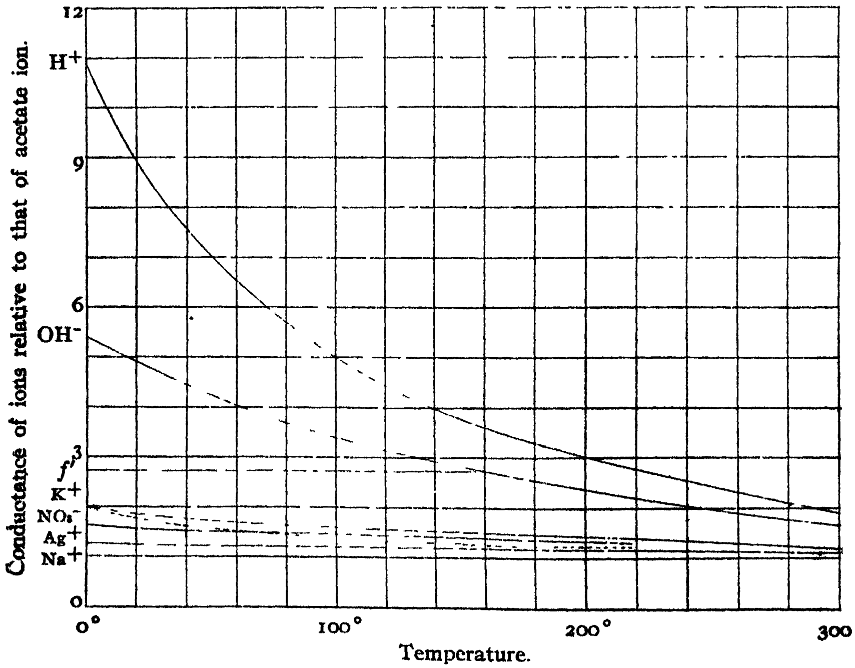

Fig. 5.—Showing relative change in ionic conductances with temperature.

It will be seen on inspection of the Table and the figure that the fluidity curve, f', is a horizontal straight line, and that the $C_2H_3O_2^-$ ion, therefore, changes its speed in proportion to the fluidity change. In the case of all the other ions the relative speed decreases with increasing fluidity and temperature. The relative decrease in speed is greater, the greater the conductance of the ion, it being greatest for the hydrogen ion and least for the sodium ion. The nitrate ion alone is exceptional, in that its relative speed decreases far more than that of other ions of the same conducting power.

From a consideration of the above results, we are led to conclude that, for very large ions, conductance and fluidity change in direct proportion to each other; but that, for ions of smaller dimensions, the speed undergoes a relatively smaller change than the fluidity of the solvent; and that this change is smaller the smaller the ion, *i. e.*, the larger the original speed of the ion.

4. Discussion.

A. Nature of the Molecular Changes Occurring in Water.

The dependence of the phenomena concerned in conductance and viscosity on the relative dimensions of the molecules of the solvent and of the ions has already been pointed out. Before proceeding farther it is necessary to consider the molecular state of water itself and the changes to which it is subject under various conditions. It is the accepted view that water consists not of single but of associated molecules, the complexity of which is a function of the temperature. As is well known, water exhibits a maximum of density in the neighborhood of 4°. This peculiar form of the density curve is readily explained on the assumption that, as the temperature falls, the volume change is the result of two factors:[1] first, a normal contraction, due to a diminution of the distance between the various molecules; and, second, an expansion due to an increase in the number and complexity of the molecular aggregates. The assumption that the aggregates occupy a space larger than that of the simple molecules is a logical one, since the density of solid water is much less than that of the liquid. These aggregates, which precipitate from solution—so to speak—when solidification occurs, are doubtless present in water even at high temperatures, although their complexity and their number is much decreased. In this connection, it may be recalled that in other cases than pure water it has been shown that crystalline aggregates persist in a liquid at temperatures far above that at which they are normally present.[2]

Since the volume of the aggregates is greater than that of the simple molecules, it follows, that if water be placed under pressure the percentage of aggregates present in water will be less than in pure water under normal pressure.

Now, the viscosity of a liquid is greatly increased by the presence of a few large aggregates. This is shown by the fact that the addition of a substance of large molecular weight increases the viscosity of a solution enormously. Such, for example, is the case when sugar is added to water. The viscosity of water at ordinary temperatures is, therefore, for the most part due to the presence of highly complex aggregates. If pressure be applied to water at a temperature not too far removed from its freezing point, the percentage of the aggregates, or the average extent of aggregation, is reduced thereby. As a result, the fluidity of water is increased with increasing pressure and decreasing volume. Of course, if the pressure be carried high enough, the viscosity must ultimately increase again, because of the reduction of the mean distance between the molecules of the liquid. At temperatures, far removed from the freezing point where the largest aggregates have already disappeared, the viscosity will not be reduced by application of pressure.

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[1] Sutherland (36).

[2] Young and Mitchell (37).

Similarly, the cause for the negative viscosity of certain solutions in water is, doubtless, the dissociation of the molecular aggregates of the liquid, the ones to which the high viscosity of water is due; and it seems highly probable that this dissociation is due to an increase of the internal pressure on the liquid as suggested by Tammann.[1] The correspondence of the viscosity-pressure curve of water with the viscosity-concentration curve of certain electrolytes (Fig. 4), both as to form and to temperature range, leaves little room for doubting that the negative viscosity of solutions is due to disgregation of the solvent aggregates.

Even in the case of electrolytes which do not exhibit negative viscosity, the disgregation effect enters, but it is combined with an increase in viscosity due to the presence of large ions or un-ionized molecules. The resulting effect, therefore, is that initially (*i. e.*, at lower concentrations) the viscosity curve rises much less rapidly than it does at higher concentrations.

The foregoing considerations account for the fact that the conductance can be corrected proportionately to the viscosity change in the case of electrolytes which exhibit negative viscosity, but not in the case of electrolytes which exhibit a large positive viscosity effect. In the case of lithium chloride, for example, the viscosity change is due to the presence of very large neutral molecules of the salt and, probably, also to large lithium ions. Now, Washburn(39) has shown that the lithium ion is much more highly hydrated than the chloride ion. The lithium ion will, therefore, experience much greater opposition to its motion than the relatively small chloride ion. If the difference in the size of the ions is great enough, the smaller ion will, in the limit, experience no change whatever in resistance to motion; while the larger ion will experience an increased resistance, which is directly proportional to the fluidity change. It is obvious that the transference number of the ions will be affected, in this case, in correspondence with the change in the speed of the larger ion.

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[1] Compare, also Euler(38).

There are many experimental observations which bear out this hypothesis. According to Denison(40) the relative speed of the anion in gelatin solutions of $SrCl_2$ is greater than in pure water. In this case only the largest ions undergo any alteration in speed in consequence of the presence of the colloid. In the case of aqueous solutions, those electrolytes whose solutions exhibit a marked positive viscosity effect likewise exhibit a marked change of their transference numbers with concentration. This change corresponds to a smaller relative speed of the more slowly moving ion. Thus, with increasing concentration the transference number of the Li^+ ion in LiCl solutions decreases, while in HCl the transference number of the Cl^- ion decreases with concentration. The change in the relative speed of the ions is thus opposite in direction to what is to be expected on the assumption that the more highly hydrated ion is losing its hydrate molecules at higher concentration. On the other hand, if we assume that the more highly hydrated ion (the larger ion) experiences a greater diminution of speed, owing to the viscosity change, than does the smaller ion, the expected change in transference numbers is in agreement with the observed results.[1]

At 1.25 normal the viscosity of pure LiCl solution is approximately 1.14 times that of pure water. Assuming that the speed of the Cl^- ion remains unchanged with increasing viscosity, but that the speed of the much larger Li^+ ion decreases in proportion to fluidity, we may calculate the transference number of the Li^+ ion at 1.25 normal. Assuming the limiting conductance of the Cl^- and Li^+ ions to be 65.5 and 33.3, respectively, we have for the transference number of the Li^+ ion at 1.25 normal the value:

$$T^{Li^+}_{1.25} = \frac{33.3/1.14}{65.5 + 33.3/1.14} = 0.304.$$

The transference number of the Li^+ ion at infinite dilution is 0.337. The change in transference number of the Li^+ ion as calculated above is smaller than the change of the ordinary transference number. This discrepancy may be due to the influence of hydration on the transference results. The curve *C* of Fig. 2 has been calculated on the assumption that the lithium ion changes its speed in direct proportion to the viscosity change. On inspection, it is apparent that a straight line results and that it is in excellent agreement with the points in the more dilute solutions, where the correction for viscosity is either very small or negligible. So far as our available data go, the observed change of transference numbers with concentration may be accounted for on the hypothesis that the viscosity change, due to the presence of large molecules, affects the speed of large and small ions in different degree, causing the greater change in the case of the larger ion.[1]

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[1] The consideration of the influence of viscosity change on the transference numbers is greatly complicated, owing to uncertainties as to the influence of hydration on the results of transference measurements. In the case of transference measurements made in the presence of a non-electrolyte uncertainties arise in consequence of the influence of the viscosity due to the added non-electrolyte on the speed of the ions.

It is at once apparent that it is not, in general, possible to correct for viscosity except in case the viscosity change is due to small molecules, as, for example, in the case of salts with negative viscosity. The changes due to hydrostatic pressure can also probably be corrected in this way. In other cases it is necessary to correct the conductance of each ion separately. From what has been said, it is obvious that the correction will be larger, the larger the ion. Washburn(42) suggested applying a viscosity correction in this manner. He assumes that the relation between viscosity and conductance for concentration change is the same as for temperature change, and employs, for the constant p of Equation I, the values for the several ions determined by Johnston from the change of conductance with temperature. It is obvious, from the preceding considerations, that the value of p deduced from temperature change is not necessarily applicable to a viscosity change due to some other agency. The constant p of Equation I is smaller, the larger the conducting power of the ion. Now it is in the case of these ions that we have solutions with negative viscosity, where the conductance change is proportional to the fluidity change, *i. e.*, p should be equal to unity as far as the concentration viscosity correction is concerned. On the other hand, in the case of a highly hydrated salt, such as LiCl, for example. The correction to be applied is much smaller than the viscosity ratio.

It is not possible to account for the change in transference numbers by assuming that the highly hydrated ions break down at higher concentrations. For, while it is true that a change in the transference number with concentration is found only in the case of highly hydrated salts, yet the change is always in a direction corresponding to a slowing up of the more highly hydrated ion, *i. e.*, the more slowly moving ion, and it is obvious that if the hydration of the larger ion decreased with increasing concentration, its speed would become relatively greater.

The fact, that the conductance of KI solutions may be corrected in direct proportion to the viscosity change up to a concentration of 5.66 normal, is practically conclusive evidence that the hydration of the K^+ and I^- ions does not change materially with concentration. This is not unexpected, since the activity of water in a normal solution is only about 2% less than that of pure water.

B. Change of Ionic Conductance with Temperature.

One of the most remarkable phenomena in connection with the conductance of aqueous solutions, and one for which no adequate explanation has heretofore been suggested, is the change of the conductance of the various ions with temperature. That the ionic conductances of the different ions are tending toward an approximately common value at higher temperatures was pointed out by Kohlrausch. The work of Noyes and his associates, in which the conductances of aqueous solutions were measured as high as 306°, has shown, beyond a doubt, that the relation pointed out by Kohlrausch at low temperatures holds equally well at high temperatures. The change of conductance with temperature is strikingly shown in Fig. 5. Whereas, at 0°, the ratio of the conductance of the hydrogen to that of the acetate ion is 10.6,[1] at 306° it is only 1.82. In other words, at 306°, the speed of the hydrogen ion, relative to that of the acetate ion, is less than that of the potassium ion, relative to the speed of the acetate ion at 0°. A change of this order can occur only as a result of some far-reaching and fundamental change of the conditions existing in the immediate neighborhood of the ions.

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[1] Compare, Arrhenius(7), p. 500, *et seq.*

Before pursuing this subject farther, it will be well to point out some other significant facts. Foremost among these is the fact that the larger the ion, *i. e.*, the smaller its conductance, the more nearly does its change of conductance with temperature change approach a linear function of the fluidity of the solvent.[2] This is shown in Table IV, and also in Fig. 5, where the fluidity line f' of the acetate ion is practically a straight, horizontal line.

It is interesting to note, in this connection, that, while the ratios Λ_0/f of the conductances of the more rapidly moving ions to the fluidity of the solvent in aqueous solutions differ greatly from the same ratios in ammonia, the ratios for the slowly moving ions are practically identical. Thus, in water the ratio Λ_0/f for the acetate ion has the value 0.367. The conductance of the acetate ion in ammonia is not known, but, if we consider that of the negative ion in cyanacetamide, we find the ratio $\Lambda_0/f = 0.346$.[3]

If the considerations, regarding the relation between viscosity and conductance, in an earlier section of this paper are correct, then the approach of the conductance of the different ions toward a common limit at higher temperatures can be explained only on the assumption that at higher temperature the dimensions of all ions approach a common limit. Now, it might be suggested that as the temperature rises the more highly hydrated ions break down and thus approach the conducting power of the less hydrated ions. This hypothesis, however, is not in agreement with a number of important facts. Thus, if the highly solvated ions increased their speed as a result of diminution of their dimensions, we should expect the conductance of these ions to increase more rapidly than in correspondence to the fluidity change of water. Such is not the case. The slowest univalent ion for which we have data over a large temperature range, namely the acetate ion, experiences a conductance change in exact proportion to the fluidity change. Similarly, the sodium ion, whose conductance is the smallest next to that of the acetate ion, experiences an increase in conductance which is smaller than that of the fluidity, but the higher the temperature the more nearly does its conductance change become proportional to that of the fluidity of pure water. The same considerations hold for all the other ions without exception, save that the smaller the ion, the less does its conductance increase in proportion to the fluidity of the solvent. If the phenomenon under consideration were due to a decrease in the hydration of the ions, we should expect the conductance of the rapidly moving ions to increase in proportion to the fluidity change, while the conductance of the larger ions should increase much more rapidly. The converse of this is actually true.

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[1] Johnston's value for the conductance of the H^+ ion gives 11.8. This number appears to be somewhat too large. The above value has been approximated from Fig. 5.

[2] Compare Kohlrausch (47).

[3] Kraus and Bray (49), p. 1343.

But even were we to deny the force of this argument, there are other considerations of equal force which show that the hydration of the ions does not decrease with increasing temperature. If we consider a system of particles moving in a medium of molecular structure, the speed of the particles under a given impressed force will vary inversely as their diameter, *i. e.*, according to Stokes' law, provided the particles are large compared with the dimensions of the molecules of the medium. If, now, we were to reduce the dimensions of all the particles, the medium remaining the same, a point would ultimately be reached where the speed of the smaller particles would increase more rapidly than that of the larger particles, and this divergence of the speed of the particles would continue until the dimensions of all the particles were small compared to those of the molecules of the medium. Now the acetate ion, even assuming it to be unhydrated, is large in comparison with a water molecule. At high temperatures the association of water decreases and the acetate ion is relatively larger in comparison. If we were to assume that all the ions lost their combined solvent at high temperatures, the difference in the speed of the different ions at 306° should be very great. In other words, with increasing temperature we should expect the different ions to approach limiting values which, instead of being the same for all ions, should differ as much as or more than those at lower temperatures.

It is evident from an examination of the experimental data that the different ions are approaching a common limit of conductance; at any rate, this is true of ions whose complexity does not exceed that of the acetate or nitrate ion. Their dimensions must, therefore, be the same. Since they can approach this condition only by adding water molecules, it follows that, with increasing temperature, the water envelopes, which probably surround all ions in aqueous solution, increase, and that the ions ultimately are all surrounded by envelopes of the same dimensions. This may at first seem an unwarranted assumption, but a careful examination discloses nothing inconsistent with known facts. If we assume that the forces concerned in the hydration of the ions are electrical in their origin, it follows that the force acting between a charge and the molecules of its surrounding envelope must be relatively independent of temperature, or even increase with it. For, since the dielectric constant of water decreases with increasing temperature, it follows that the field of force about a charge increases. If, then, an equilibrium exists between the ions and the solvent, the degree of hydration of the ions will increase with temperature. Another way of looking at the same phenomenon is to consider the solvent as a highly associated liquid. Let us assume that the water molecules are added to an ion, not as aggregates, but as single molecules. At low temperatures, where the association of the liquid is high, the number of single water molecules present will be relatively small and the envelope surrounding an ion will be small. At higher temperatures, however, the association of the solvent decreases, the proportion of single molecules increases and the degree of solvation of the ions increases. At low temperatures only those ions will be highly hydrated which exhibit a strong tendency to form solvates in the free salt. At high temperatures, however, the purely electrical forces become more and more determinative of solvation and consequently all ions approach each other in size.

C. The Hydrogen and Hydroxyl Ions.

The preceding considerations have a bearing on questions regarding the large difference in the speed of the various ions in water. Nonaqueous solvents have much smaller dielectric constants and are much less associated than water. Therefore, the solvent envelope will, in general, be larger and the different ions will approach each other more nearly in speed. Because of the high degree of association of water, some ions lose their envelopes in a very large measure, the resulting ion becomes small in comparison with the solvent molecules and an abnormally high speed results. The hydrogen and hydroxyl ions are examples of ions of this type.

It has been a commonly accepted hypothesis that the abnormally high speed of the hydrogen and hydroxyl ions bears some relation to the fact that these ions result when water itself dissociates.[1] Kraus and Bray,[2] however, have shown that the NH_4^+ and the NH_2^- ions in ammonia, which bear the same relation to ammonia as the H^+ and OH^- ions do to water, possess, in ammonia, a conductance far below the average. Further, and this is most important, the H^+ and OH^- ions in water exhibit exceptional speed in far smaller degree at high than at low temperature. If any relation existed between the abnormally high conductance of these ions and the dissociation of water, we should expect these ions to become more exceptional as the dissociation of water increases.

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[1] Danneel(48).

[2] Kraus and Bray(49), pp. 1368–9.

The conception underlying this hypothesis, which seeks to connect the high conductance values of H^+ and OH^- ions with the dissociation of water, embodies some elements of the so-called "Grotthuss Theory," according to which conductance takes place by an interchange of H^+ and OH^- ions with the water molecules between the electrodes along the lines of current flow. If this theory were true, we should certainly expect the effect to become more pronounced at higher temperatures, which it does not.

There has been a discrepancy between the values of the transference number for the H^+ ion, as determined by conductance and transference measurements. The value for the transference number of H^+ in hydrochloric acid has, in most cases, been found larger by transference than by conductance measurements, even in dilute solutions. Lewis(43) has recently cited this intance as showing that the speed of the ions may change with concentration, even in relatively dilute solutions. It is, of course, obvious that the conductance method can not give correct values of the ionization when the transference number changes. The reason for the observed changes in transference numbers I have already given. In the case of the hydrogen ion, certain circumstances have operated to lead to a seeming disagreement. In a recent paper, Kraus and Bray have shown that the Λ_0 value for KCl, as commonly accepted, is too high by several units.[1] This discrepancy is due to the uncertainty in correction for the conductance of the solvent in dilute solution, and likewise to the use of a method of extrapolation for Λ_0 which is inapplicable. In the case of the acids, these sources of error have not been operative to the same extent as in that of the salts. Therefore, the commonly accepted value for the conductance of the hydrogen ion is more nearly correct than it is for other ions. Kendall(44) has recently determined the conductance of the hydrogen ion at 25° to be 347.0. At 18° this gives a value of 312.6. If we take for the conductance of the chlorine ion, instead of the value 65.5, the lower value 64.4 deduced from the Λ_0 of KCl as found by Kraus and Bray, we obtain for the transference number of the H^+ ion in hydrochloric acid the value 0.830. This is in excellent agreement with the value obtained by Noyes and Kato(45), in dilute solutions by direct determination, and also with the results of Drucker(46). Actually, therefore, no discrepancy exists, and the transference number of the ions in HCl undergo only a small change even up to fairly high concentrations.

[1] P. 1407, *et seq.* of reference 49.

D. Speed of the Ions in Different Solvents.

If the forces governing the solvation of the ions are electrical rather than chemical in their origin, we have a ready explanation for the fact, that in different solvents the ratio Λ_0/f of conductance to fluidity has approximately the same value in different solvents. For the electrical forces are in all cases approximately the same for different solvent media, as well as for different ions. The envelope will, therefore, be large in all cases and relatively independent of the nature of the solvent.

It is interesting to compare the speed of the ordinary ions in water and ammonia with that of the ions produced in hexane by radiations. In Table V the name of the solvent appears in the first column, that of the ion in the second column, the absolute speed, S, of the ion $\times 10^4$ in the third column, the fluidity f in the fourth column, and in the last column the ratio $S/f \times 10^6$. The values in hexane are due to Jaffé(21).

TABLE V.—SPEED OF IONS IN DIFFERENT SOLVENTS.

Solvent	Ion	$S \times 10^4$	f.	$S/f \times 10^6$.
H_2O	Acetate	3.58	95.35	3.76
NH_3	Lithium	11.60	376	3.05
Hexane	Positive	6.03	312	1.98
Hexane	Negative	4.17	312	1.34

The speed of the positive and negative ions produced by radiations of radioactive substances in hexane is, therefore, a little less, relative to fluidity, than that of the slowest ions in ammonia or water. Since these ions in ammonia and water are very large, it follows that a single charge in hexane must be combined with a considerable number of solvent molecules.

E. Non-aqueous Solutions.

Examination of Fig. 3 shows that the mobility of the ions in ammonia changes less than the fluidity of the solvent. This is not surprising, since both the K^+ and I^- ions in ammonia possess relatively high mobilities. In this connection, it is of importance to note that the viscosity change due to the presence of the salt is enormously greater for non-aqueous solvents than for water. This is illustrated in Table VI.

TABLE VI.—VISCOSITY OF SOLUTIONS IN DIFFERENT SOLVENTS.

		Relative viscosity at concentration.		
Solvent.	Solute.	0.5.	1.0.	2.5
Water	LiCl	1.05	1.10	1.42
Ammonia	KI	1.16	1.38	2.38
Methylamine	$AgNO_3$	1.40	1.96	6.38

In the first column appears the name of the solvent, in the second the name of the solute, and in the third, fourth and fifth columns, respectively, the relative viscosities of the solutions at 0.5, 1.0 and 2.5 normal. As aqueous solutions go, the viscosity of lithium chloride solutions is very large. Yet, as is apparent from the table, the viscosity of KI in ammonia is enormously greater than that of LiCl in water. Values are also given for the viscosity of solutions of $AgNO_3$ in methylamine. As may be seen, the viscosity of silver nitrate solutions in methylamine is far greater than that of KI in ammonia. The viscosities of other inorganic salts, in ammonia and methylamine, do not differ greatly from those of the salts given in the table.[1]

According to considerations already set forth in this paper, the relative dimensions of the ions and solvent molecules do not differ greatly in different solvents; although in water at low temperatures the ions are, relatively, somewhat smaller than in the solvents. It follows, therefore, that the viscosity change in ammonia solutions is due to molecules which are relatively very large. Probably the viscosity change is due to molecules of the un-ionized salt associated with a large number of solvent molecules.[2] If this is the case, then we should expect the speed of the ions in ammonia to be affected less, due to concentration change, than in water. This explains why Equation IV holds for non-aqueous solvents to such high concentrations, as Kraus and Bray have shown. The tendency of the dissolved salt to form large aggregates with the solvent apparently increases with decreasing dielectric constant. In non-aqueous solvents, then, we can not hope to apply a correction for the viscosity of the solvent. On the other hand, we are justified in assuming that no correction is necessary so long as Equation IV holds. The fall in the conductance curves of concentrated non-aqueous solutions, with increasing concentrations, is undoubtedly due to the influence of the increasing viscosity of the solutions.

F. The Calculation of Molecular Dimensions.

A number of writers have attempted to determine the dimensions of ions and dissolved molecules from conductance and diffusion experiments. The equations which are employed for this purpose involve a knowledge of the molecular weight or the density of the particles in question. For this purpose the densities of the salts in the solid or liquid state have been employed. In the light of the present investigation, it is obvious that we have no knowledge of the density of the ions or of dissolved substances, in general; nor do we possess a knowledge of their molecular weights save in a few instances. Calculations of this kind are entirely futile and their results are misleading.

G. Deviation from the Mass-Action Law and Change of Ionic Mobilities.

One of the important problems confronting the further development of the theory of electrolytic solutions is the question whether the conductance method gives a correct measure of the ionization in dilute solutions, *i. e.*, where viscosity and other similar effects are negligible. As is well known, the ionization values, as calculated from conductance data, do not satisfy the law of mass action. This may be due to the fact that the mobility of the ions is not independent of the concentration, as was first pointed out by Ostwald. There has been much controversy regarding the applicability of the conductance method as a measure of ionization without, however, leading to any definite results. In a recent paper, Lewis(43) reverts to this question and suggests that in aqueous solution the mobility of the ions is a function of concentration, but he makes a reservation to the effect that in other solutions, particularly non-aqueous solutions, it may be necessary to make the additional hypothesis that a real deviation from the mass-action law exists.

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[1] Fitzgerald(30).

[2] It is to be noted that in solvents of lower dielectric constant, the proportion of un-ionized molecules is relatively much greater than in water.

The results of the present paper have an important bearing on this question, for it has been shown that solutions in water obey Equation II, which is a special case of Equation IV, to concentrations greater than 5.0 normal. Now, Kraus and Bray(49) have shown that this equation is quantitatively applicable to all non-aqueous solutions for which accurate data are available. It is clear, therefore, that the nature of the deviation of the actual conductance curve from that required by the mass-action law is precisely the same whether the solutions be aqueous or non-aqueous. Any explanation for the observed discrepancies must, therefore, be generally applicable to all solvents without exceptions, otherwise it must fall to the ground.

If the mass-action law holds at high concentrations, then Equation IV expresses the relation between the change of ionic mobility and concentration. On this hypothesis it is evident that according to equation IV the mobilities of both ions change with concentration in exactly the same manner. For, in Equation IV, Λ_o, the sum of the ionic conductances enters, and not the individual ionic conductances. When combined with a given positive ion, M^+, for example, the negative ion X^- follows the same law of change of speed as the ion M^+. When however, the ion X^- is combined with another positive ion $M_1{}^+$, it follows an entirely new law of conductance change which, in this case, is the same for $M_1{}^+$ and X^-; for the constants of Equation IV for the two salts MX and M_1X will, in general, be different and this difference is often large. If we grant the correctness of the law of the independent motion of the ions, then it is obvious that the hypothesis which assumes the mobility of the ions to change with concentration becomes untenable.

Other considerations, also, go to show that the hypothesis of increasing ionic mobilities is incorrect. If the speed of the ions increases with increasing concentration, then this increase in speed can only be ascribed to a diminution in the size of the ions; for the increase in speed can not be due to increased fluidity, since the fluidity in general decreases and ultimately reduces the speed of the ions, as has been shown above. Now the increase in speed which would have to be assumed in certain non-aqueous solutions is as much as 1000-fold. A diminution of the dimensions of the ions of a magnitude sufficient to account for this order of change in speed is too improbable to warrant serious consideration. Even if we were to grant that such change in dimensions took place, we would only meet with another inconsistency, since, if the dimensions of the ions were reduced to this extent, their motion should become practically independent of the viscosity of the solution, which is manifestly due to the presence of large molecules or aggregate. We have seen, however, that in all cases in concentrated solutions, the conductance ultimately decreases with increasing concentration, as a result of increasing viscosity. Finally, it should be noted that, although a large number of electrolytes have been investigated in many different solvents, no case has ever been discovered where the ratio Λ/Λ_0 exceeds unity in concentrated solutions. If the mobility of the ions increases with concentration, we might well expect to find, at least, some instances in which the speed increases to such extent that the ratio Λ/Λ_0 exceeded unity. This would indeed be a crucial test in favor of the hypothesis in question.

One other point remains to be considered; the mobility of the ions may remain unaltered with concentration change, the deviation from the law of mass action being due to the superposition on the normal ionic conduction process of another type of conduction which, for example, might be of the nature of a "Grotthuss chain" effect. Whatever the nature of such a process might be, it must manifestly be ionic in character, since, at the electrodes, Faraday's laws hold for the electrochemical change accompanying the current. That the solvent itself takes any direct part in the conduction process is extremely unlikely; for the deviation from the law of mass action is not a function of the chemical properties of the solvent, but rather of its physical properties, the dielectric constant in particular. We thus find deviations of the same order of magnitude in solvents having the same dielectric constant; whether the solvent be elementary in its nature, or whether a compound, whether the solvent be readily dissociable into ions, or whether it be a compound which is entirely neutral in its properties. The deviation, moreover, is a direct function not of the concentration of the un-ionized fraction, but of the ions. The observed results can not, therefore, be explained by means of a "Grotthuss chain" effect through the un-ionized molecules.

As we have seen, the hypotheses which seek to account for the deviations from the mass-action law by assuming that the ratio Λ/Λ_0 does not give the correct degree of ionization lead to conclusions which are not in accord with the facts. In contrast to these, the hypothesis, that the ratio Λ/Λ_0 gives the correct ionization, accounts for all the known facts in a simple manner and without conflict with any theoretical principle. In dilute solutions, as Kraus and Bray have shown, the mass-action law applies in all cases. That deviations from the mass-action law should arise at higher concentrations is a result which was to have been expected, since the applicability of this law postulates that the forces acting between molecules of different species or of the same species are negligible. That large forces come into play in the neighborhood of the ions is evidenced by the extent to which the ions are surrounded with solvent molecules. There is no consideration which, at the present time, would enable us to predict at what concentration the forces between the individual particles of an electrolytic system become negligible. The assumption that these disturbing forces would begin to become negligible in the neighborhood of 0.1 normal concentration as they do in non-electrolytic systems is entirely unwarranted. The only means we now have for determining at what concentration the disturbing forces between the particles become negligible is that of direct experiment. The results of such experiments have shown that the influence of the forces between the particles in an electrolytic system is, in most cases, appreciable even beyond a concentration of 0.001 normal, and that, as was to have been expected, the deviation from the mass-action law is, in general, smaller the higher the dielectric constant of the medium. The original assumption of Arrhenius that the ratio Λ/Λ_0 measures the true degree of ionization is borne out by the facts; and the future problem of the theory of electrolytic solutions is to develop an adequate theory for the equilibrium of charged systems.

5. Summary.

The general principles governing conductance as a function of viscosity change are discussed.

It is shown that in the case of aqueous solutions exhibiting negative viscosity, the conductance may be corrected for viscosity in direct proportion to the fluidity change. The same is probably true for viscosity change due to external pressure.

In the case of aqueous solutions exhibiting a positive viscosity, correction for viscosity can not in general be made, although in some instances, correction may perhaps be effected by considering the influence of viscosity on the individual ions.

The change in the true transference numbers of electrolytes with concentration is due to the different effect of viscosity on the speed of the two ions.

The viscosity change due to concentration change in non-aqueous solutions is positive and much greater than it is in water for inorganic electrolytes. The speed of the ions in non-aqueous solutions changes far less than the fluidity of the solutions, although at high concentrations a marked influence results. Correction for viscosity, so far, is not possible in these cases, and up to normal concentration a correction is in many cases unnecessary.

The influence of viscosity on the speed of the ions is governed by the relative dimensions of the ions and the molecules to which viscosity change is due. The characteristic relations observed in the case of aqueous solutions are due, in part at least, to the complexity of the molecules of liquid water.

At higher temperatures the speeds of different ions in aqueous solutions approach, approximately, a common limit, indicating that the ions, under these conditions, are approaching one another in size.

It is shown that the dimensional changes observed can not be accounted for on the assumption that the larger ions become smaller at higher temperatures; and it is suggested that the smaller ions increase in size (due to increasing hydration) with increasing temperature. This increase in dimensions is due to the decrease in the value of the dielectric constant with increasing temperature and probably also to decreasing complexity of the water molecules.

It is shown that the commonly accepted hypothesis, according to which the high speed of the hydrogen and hydroxyl ion is related to the fact that these ions are ions of the solvent itself, is not true.

The facts discussed in this paper corroborate the fundamental hypothesis of Arrhenius that the degree of ionization of electrolytes is correctly measured by the conductance ratio, Λ/Λ_0.

LIST OF REFERENCES.

1. G. Wiedemann, *Pogg. Ann.*, **99**, 228 (1856).
2. Grotian, *Wied. Ann.*, **160**, 238 (1877); **8**, 259 (1879).
3. Stephan, *Wied. Ann.*, **17**, 673 (1882).
4. Kohlrausch, *Wied. Ann.*, **6**, p. 160, *et seq.* (1879).
5. Arrhenius, *Z. physik. Chem.*, **1**, 631 (1887).
6. Ostwald, *Z. physik. Chem.*, **2**, 282 (1888).
7. Arrhenius, *Z. physik. Chem.*, **9**, 487 (1892).
8. Walden, *Z. physik. Chem* , **55**, 246 (1906).
9. Martin and Masson, *J. Chem. Soc.*, **79**, 707 (1901).
10. Jones, *et al*, Carnegie Publication, No. 80.
11. Fawsitt, *Proc. Roy. Soc. Edin.*, **25**, 51 (1903).
12. Hartley, Thomas and Appleby, *J. Chem. Soc.*, **93**, 538 (1908).
13. Green, *J. Chem. Soc.*, **93**, 2049 (1908).
14. Bonsfield, *Z. physik. Chem.*, **53**, 257 (1903).
15. R. Lorenz, *Z. physik. Chem.*, **78**, 257 (1911).
16. Herzog, *Z. Electrochem.*, **16**, 1003 (1910).
17. Johnston, THIS JOURNAL, **31**, 1010 (1909).
18. Noyes, *et al*, Carnegie Publication, No. 63.
19. Washburn, THIS JOURNAL, **33**, 1461 (1911).
20. Millikan, *Phys. Rev.*, 349 (1911).
21. Jaffé, *Ann. d. Physik*, **32**, 148 (1910).

22. Storch, *Z. physik. Chem.*, **19,** 13 (1896).
23. Bray, *Trans. Am. Electrochem. Soc.*, **21,** 143 (1912).
24. Sloan, THIS JOURNAL, **32,** 946 (1910).
25. Kahlenberg, *J. physic. Chem.*, **5,** 339 (1901).
26. Washburn and MacInness, THIS JOURNAL, **33,** 1686 (1911)
27. Sprung, *Wied. Ann.*, **159,** 1 (1876).
28. Franklin and Kraus, *Am. Chem. J.*, **23,** 277 (1900); THIS JOURNAL, **27,** 191 (1901).
29. Franklin, *Z. physik. Chem.*, **69,** 272 (1909).
30. Fitzgerald, *J Phys. Chem.*, **16,** 621 (1912).
31. Franklin and Gibbs, THIS JOURNAL, **29,** 1389 (1907).
32. Franklin, *J. Phys. Chem.*, **15,** 675 (1911).
33. Tammann, *Wied. Ann.*, **69,** 770 (1899).
34. Cohen, *Wied. Ann.*, **45,** 666 (1892).
35. Kohlrausch, *Wied. Ann.*, **6,** 196 (1879).
36. Sutherland, *Phil. Mag.*, **50,** 460 (1900).
37. Young and Mitchell, THIS JOURNAL, **26,** 1389 (1904).
38. Euler, *Z. physik. Chem.*, **25,** 536 (1898).
39. Washburn, THIS JOURNAL, **31,** 322 (1909).
40. Denison, *Z. physik. Chem.*, **43,** 596 (1903).
41. Buchbök, *Z. physik. Chem.*, **55,** 563 (1906).
42. Washburn, THIS JOURNAL, **33,** 1461 (1911).
43. Lewis, THIS JOURNAL, **34,** 1631 (1912).
44. Kendall, *J. Chem. Soc.*, **102,** 1275 (1912).
45. Noyes and Kato, THIS JOURNAL, **30,** 318 (1908)
46. Drucker, *Z. physik Chem.*, **62,** 731 (1908).
47. Kohlrausch, *Proc Roy. Soc*, **71,** 338 (1903)
48. Danneel, *Z. Electrochem.*, **11,** 249 (1905).
49. Kraus and Bray, THIS JOURNAL, **35,** 1315 (1913).

BOSTON, MASS.

CALIBRATION TABLES FOR COPPER-CONSTANTAN AND PLATINUM-PLATINRHODIUM THERMOELEMENTS.

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In view of the fact that chemists are making more and more extensive use of thermoelements as a means of measuring high temperatures, it seemed desirable to present two tables which save much trouble in converting microvolts into degrees. Nothing will be said here as to the precautions to be observed in the use of thermoelements,[1] further than that experience has shown the necessity of frequent recalibration in order to insure trustworthy results. The experimental work required for such a calibration involves comparatively little time or labor, but interpolation between the fixed points can be accomplished accurately only by means of an empirical equation expressing the relation between electromotive force and temperature, and repeated recalculation of such an equation may prove a somewhat tiresome task. This may be avoided by the use of a table representing a standard curve in conjunction with an appropriate "deviation curve"; the advantages of this procedure have already been pointed out by Sosman.[1] Such standard curves are arbitrary, but it is always advisable, for the sake of accuracy, that they represent closely the actual form of curve characteristic of the thermoelement, so that the deviations may be as small as possible.

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[1] These precautions have been discussed by W. P. White, *Physic. Rev.*, **23,** 449 (1906); *Am. J. Sci.*, [4] **28,** 479 (1909).

Standard curves for use with platinum-platinrhodium[2] and copper-constantan[3] elements have been given in previous publications; but they now require amendment. Certain changes in the accepted temperature scale below 650° have necessitated a recalculation for the curve for the Pt-PtRh couple; and the superior qualities of the kind of constantan wire, which we have lately succeeded in obtaining, made it desirable to construct for copper-constantan elements a new table which should conform more closely to the actual observations with that kind of wire.

The Copper-constantan Curve.—(Table I.) The curve given in Table I represents very closely the observations for a sample of "Ideal" wire.[4] This wire is of such uniformity—a characteristic which is very desirable—that three lengths cut from the same spool did not differ in electromotive force against copper by as much as 1 part in 15,000.

The table was calculated from the equation

$$\mathbf{E} = 74.672t - 13892\ (1 - e^{-0.00261t}).$$

E being the electromotive force in microvolts, t the temperature (Centigrade) and e the base of the natural logarithms. The advantages of this form of equation, as compared with the ordinary power series, have been indicated in another paper;[5] that it is capable of reproducing the observations with high precision is evident from the following:

Temp.	**E** (obs.) Microvolts.	**E** (calc.) Microvolts.	Difference. Microvolts.[6]
24.30	961.1	960.9	0.2
49.59	2010.9	2010.8	0.1
78.75	2391.7	3291.4	0.3
100.0	4276.	(4276) *	...
217.95	10248	(10248) *	...
305.9	15203.	(15203) *	...

[1] R. B. Sosman, *Am. J. Sci.*, [4] **30**, 7 (1910).

[2] *Ibid.*, [4] **30**, 9 (1910).

[3] L. H. Adams and J. Johnston, *Am. J. Sci.*, [4] **32**, 534 (1912).

[4] Practically identical with constantan. Obtainable from the Electrical Alloys Co., Morristown, N. J.; size No. 30 B. & S., double silk-covered, is perhaps the most convenient.

[5] L. H. Adams, *J. Wash. Acad.*, **3**, 469 (1913).

[6] 1 microvolt corresponds in this case to about 0.02°.

* Used in computing the equation.

The Pt-PtRh Curve.—(Table II.) For this element it proved impossible to find a single equation, with a reasonable number of constants, which would adequately express the relation between temperature and electromotive force over the whole range between 0° and 1755°, the melting point of platinum; a circumstance which is hardly surprising, in view of the magnitude of the range. Accordingly, the curve given in Table II was calculated in three overlapping sections: 0–400°, 300–1200°, 1100–1755°. The first section was computed from an exponential equation of the form,

$$\mathbf{E} = At + B(1 - e^{Ct});$$

the second from the equation,[1]

$$\mathbf{E} = -308 + 8.2294t + 0.001649t^2;$$

and the third by inverting the table of Sosman[2] so that the argument is in microvolts and not degrees. That this procedure introduced in this case no discontinuities in the slope of the curve at the points of transition from one section to another, was established by the identity of the results calculated in both ways for the overlapping portions. Any slight inequalities were evened out by adjustment of the successive differences.

Remarks.—It is understood, of course, that the cold junction is maintained at 0°, which is most conveniently done by means of a mixture of ice and water contained in a vacuum-jacketed flask; if the cold junction is not at 0°, corrections similar to those given in the table by Foote must be applied.[3]

The standard temperatures employed are based mainly upon the series of gas thermometer determinations made by Day and Sosman;[4] this scale does not differ materially from that advocated by the Bureau of Standards[5] or from that now in use at the Reichsanstalt up to 1100°,[6] and it is little likely to undergo any marked change for some time to come. The tables give temperatures (on the thermodynamic scale) and temperature differences for each 100 microvolts up to the limit of usefulness of each thermoelement; this form of table is more troublesome to calculate but is much more convenient to use. The last digit in each temperature value is given mainly for purposes of interpolation; otherwise it is meaning-

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[1] A. L. Day and R. B. Sosman, *Am. J. Sci.*, [4] **33**, 528 (1912); *Ann. Physik*, **38**, 863 (1912).

[2] R. B. Sosman, *Am. J. Sci.*, [4] **30**, 9 (1910); *Carnegie Inst. Wash.*, *Pub.* **157**, 118.

[3] P. D. Foote, *Met. Chem. Eng.*, **11** 329 (1913).

[4] Arthur L. Day and R. B. Sosman, *Am. J Sci.*, [4] **29**, 93–161 (1910); **33**, 517–533 (1912); "High Temperature Gas Thermometry," *Carnegie Inst Wash.*, *Pub.* **157**; *Jour. Physique*, [5] **2**, 727, 831, 899 (1912).

[5] See G. K. Burgess, *Report 8th Intern. Congr. Appl. Chem.*, **22**, 53–63; *J. chim. phys.*, **11**, 529 (1913).

[6] It should be remarked, however, that the official calibrations issued by the Reichsanstalt are, so far as we know, still based on their old temperature scale, which at 1000° leads to temperature values about 1.5° higher than those given here.

TABLE

E.	0.		1000.		2000.		3000.		4000.	
0	0		25.27		49.20		72.08		94.07	
		2.60		2.45		2.33		2.23		2.16
100	2.60		27.72		51.53		74 31		96.23	
		2.57		2.43		2.32		2.23		2.15
200	5.17		30.15		53.85		76.54		98.38	
		2.56		2.42		2.31		2.22		2.14
300	7.73		32.57		56.16		78.76		100.52	
		2.55		2.41		2.30		2.21		2.14
400	10.28		34.98		58.46		80.97		102.66	
		2.53		2.40		2.30		2.20		2.13
500	12.81		37.38		60.76		83.17		104.79	
		2.52		2.39		2.28		2.20		2.12
600	15.33		39.77		63.04		85.37		106.91	
		2.50		2.38		2.27		2.19		2.11
700	17.83		42 15		65.31		87.56		109.02	
		2.49		2.36		2.27		2.18		2.10
800	20.32		44.51		67.58		89.74		111.12	
		2.48		2.35		2.25		2.17		2.10
900	22.80		46.86		69.83		91.91		113.22	
		2.47		2.34		2.25		2.16		2.09
1000	25.27		49.20		72 08		94.07		115.31	

E.	10000.		11000.		12000.		13000.		14000.	
0	213.36		231.74		249.82		267.60		285.13	
		1.85		1.82		1.79		1.76		1.74
100	215.21		233.56		251.61		269.36		286.87	
		1.85		1.82		1.79		1.76		1.74
200	217.06		235.38		253.40		271.12		288.61	
		1.85		1.82		1.78		1.76		1.74
300	218.91		237.20		255.18		272.88		290.35	
		1.84		1.81		1.78		1.76		1.73
400	220.75		239.01		256.96		274.64		292.08	
		1.84		1.81		1.78		1.76		1.73
500	222.59		240.82		258.74		276.40		293.81	
		1.84		1.81		1.78		1.75		1.73
600	224.43		242.63		260.52		278.15		295.54	
		1.83		1.80		1.77		1.75		1.72
700	226.26		244.43		262.29		279.90		297.26	
		1.83		1.80		1.77		1 75		1.72
800	228.09		246.23		264.06		281.65		298.98	
		1.83		1.80		1.77		1.74		1.72
900	229.92		248.03		265.83		283.39		300.70	
		1.82		1.79		1.77		1 74		1.72
1000	231.74		249.82		267.60		285.13		302 42	

Standard calibration curve for copper-constantan thermo-element giving the tem-
For use in conjunction with a deviation curve determined by calibration of the

Water	b. p.
Naphthalene	b. p.
Sn	m. p.
Benzophenone	b. p.
Cd	m. p.

I.

5000.		6000.		7000.		8000.		9000.		E.
115.31	*2.09*	135.91	*2.03*	155.95	*1.97*	175.50	*1.93*	194.62	*1.89*	0
117.40	*2.08*	137.94	*2.02*	157.92	*1.97*	177.43	*1.93*	196.51	*1.89*	100
119.48	*2.08*	139.96	*1.92*	159.89	*1.97*	179.36	*1.92*	198.40	*1.88*	200
121.56	*2.07*	141.98	*2.01*	161.86	*1.96*	181.28	*1.92*	200.28	*1.88*	300
123.63	*2.06*	143.99	*2.01*	163.82	*1.96*	183.20	*1.91*	202.16	*1.88*	400
125.69	*2.06*	146.00	*2.00*	165.78	*1.95*	185.11	*1.91*	204.04	*1.87*	500
127.75	*2.05*	148.00	*2.00*	167.73	*1.95*	187.02	*1.91*	205.91	*1.87*	600
129.80	*2.04*	150.00	*1.99*	169.68	*1.94*	188.93	*1.90*	207.78	*1.86*	700
131.84	*2.04*	151.99	*1.99*	171.62	*1.94*	190.83	*1.90*	209.64	*1.86*	800
133.88	*2.03*	153.97	*1.98*	173.56	*1.94*	192.73	*1.89*	211.50	*1.86*	900
135.91		155.95		175.50		194.62		213.36		1000

15000.		16000.		17000.		18000.	E.
302.42	*1.72*	319.49	*1.70*	336.36	*1.68*	353.09	0
304.14	*1.71*	321.19	*1.69*	338.04	*1.68*		100
305.85	*1.71*	322.88	*1.69*	339.72	*1.68*		200
307.56	*1.71*	324.57	*1.69*	341.40	*1.67*		300
309.27	*1.71*	326.26	*1.69*	343.07	*1.67*		400
310.98	*1.71*	327.95	*1.69*	344.74	*1.67*		500
312.69	*1.70*	329.64	*1.68*	346.41	*1.67*		600
314.39	*1.70*	331.32	*1.68*	348.08	*1.67*		700
316.09	*1.70*	333.00	*1.68*	349.75	*1.67*		800
317.79	*1.70*	334.68	*1.68*	351.42	*1.67*		900
319.49		336.36		353.09			1000

perature and temperature differences for every 100 microvolts. Cold junction at 0°
particular element at some of the following fixed points:

100°	4276 μv
217.95°	10248 μv
231.9°	11009 μv
305.9°	15203 μv
320.9°	16083 μv

TABLE

E.	0.		1000.		2000.		3000.		4000.	
0	0		147.1		265.4		374.3		478.1	
		17.8		*12.6*		*11.2*		*10.6*		*10.2*
100	17.8		159.7		276.6		384.9		488.3	
		16.7		*12.4*		*11.1*		*10.5*		*10.1*
200	34.5		172.1		287.7		395.4		498.4	
		15.8		*12.3*		*11.0*		*10.5*		*10.1*
300	50.3		184.3		298.7		405.9		508.5	
		15.1		*12.0*		*11.0*		*10.4*		*10.1*
400	65.4		196.3		309.7		416.3		518.6	
		14.6		*11.8*		*10.9*		*10.4*		*10.0*
500	80.0		208.1		320.6		426.7		528.6	
		14.1		*11.6*		*10.9*		*10.4*		*10.0*
600	94.1		219.7		331.5		437.1		538.6	
		13.7		*11.5*		*10.8*		*10.3*		*10.0*
700	107.8		231.2		342.3		447.4		548.6	
		13.4		*11.5*		*10.7*		*10.3*		*9.9*
800	121.2		242.7		353.0		457.7		558.5	
		13.1		*11.4*		*10.7*		*10.2*		*9.9*
900	134.3		254.1		363.7		467.9		568.4	
		12.8		*11.3*		*10.6*		*10.2*		*9.9*
1000	147.1		265.4		374.3		478.1		578.3	

E.	10000.		11000.		12000.		13000.		14000.	
0	1037.3		1122.2		1205.9		1289.3		1372.4	
		8.6		*8.4*		*8.3*		*8.4*		*8.3*
100	1045.9		1130.6		1214.2		1297.7		1380.7	
		8.5		*8.4*		*8.4*		*8.3*		*8.3*
200	1054.4		1139.0		1222.6		1306.0		1389.0	
		8.5		*8.4*		*8.3*		*8.3*		*8.3*
300	1062.9		1147.4		1230.9		1314.3		1397.3	
		8.5		*8.4*		*8.4*		*8.3*		*8.3*
400	1071.4		1155.8		1239.3		1322.6		1405.6	
		8.5		*8.4*		*8.3*		*8.3*		*8.2*
500	1079.9		1164.2		1247.6		1330.9		1413.8	
		8.5		*8.3*		*8.3*		*8.3*		*8.2*
600	1088.4		1172.5		1255.9		1339.2		1422.0	
		8.5		*8.4*		*8.4*		*8.3*		*8.2*
700	1096.9		1180.9		1264.3		1347.5		1430.2	
		8.5		*8.3*		*8.3*		*8.3*		*8.2*
800	1105.4		1189.2		1272.6		1355.8		1438.4	
		8.4		*8.4*		*8.4*		*8.3*		*8.2*
900	1113.8		1197.6		1281.0		1364.1		1446.6	
		8.4		*8.3*		*8.3*		*8.3*		*8.2*
1000	1122.2		1205.9		1289.3		1372.4		1454.8	

Standard calibration curve for Pt-Pt.Rh (10% Rh) thermoelement, giving the tem-
For use in conjunction with a deviation curve determined by calibration of the

Water	b. p.	100°	643 μv
Naphthalene	b. p.	217.95°	1585 μv
Sn	m. p.	231.9°	1706 μv
Benzophenone	b. p.	305.9°	2365 μv
Cd	m. p.	320.9°	2503 μv
Zn	m. p.	419.4°	3430 μv
Sulfur	b. p.	444.5_5°	3672 μv
Sb	m. p.	630.0°	5530 μv
Al	m. p.	658.7°	5827 μv

II.

5000.	6000.	7000.	8000.	9000.	E.
578.3	675.3	769.5	861.1	950.4	0
9.8	*9.5*	*9.3*	*9.0*	*8.8*	
588.1	684.8	778.8	870.1	959.2	100
9.8	*9.5*	*9.2*	*9.0*	*8.8*	
597.9	694.3	788.0	879.1	968.0	200
9.8	*9.5*	*9.2*	*9.0*	*8.7*	
607.7	703.8	797.2	888.1	976.7	300
9.7	*9.5*	*9.2*	*9.0*	*8.7*	
617.4	713.3	806.4	897.1	985.4	400
9.7	*9.4*	*9.2*	*9.0*	*8.7*	
627.1	722.7	815.6	906.1	994.1	500
9.7	*9.4*	*9.1*	*8.9*	*8.7*	
636.8	732.1	824.7	915.0	1002.8	600
9.7	*9.4*	*9.1*	*8.9*	*8.7*	
646.5	741.5	833.8	923.9	1011.5	700
9.6	*9.4*	*9.1*	*8.9*	*8.6*	
656.1	750.9	842.9	932.8	1020.1	800
9.6	*9.3*	*9.1*	*8.8*	*8.6*	
665.7	760.2	852.0	941.6	1028.7	900
9.6	*9.3*	*9.1*	*8.8*	*8.6*	
675.3	769.5	861.1	950.4	1037.3	1000

15000.	16000.	17000.	18000.		E.
1454.8	1537.5	1620.9	1704.3	. .	0
8.2	*8.3*	*8.3*	*8.3*		
1463.0	1545.8	1629.2	1712.6		100
8.2	*8.3*	*8.4*	*8.4*		
1471.2	1554.1	1637.6	1721.0	. . .	200
8.2	*8.3*	*8.3*	*8.3*		
1479.4	1562.4	1645.9	1729.3	.	300
8.3	*8.4*	*8.4*	*8.4*		
1487.7	1570.8	1654.3	1737.7	. . .	400
8.3	*8.3*	*8.3*	*8.3*	.	
1496.0	1579.1	1662.6	1746.0	. . .	500
8.3	*8.4*	*8.3*	*8.3*	. . .	
1504.3	1587.5	1670.9	1754.3	. . .	600
8.3	*8.3*	*8.4*	. . .	. . .	
1512.6	1595.8	1679.3	. . .	. . .	700
8.3	*8.4*	*8.3*	. . .	. .	
1520.9	1604.2	1687.6	. .	. . .	800
8.3	*8.3*	*8.4*	. . .	. . .	
1529.2	1612.5	1696.0	. . .	. . . .	900
8.3	*8.4*	*8.3*	. . .	. . .	
1537.5	1620.9	1704.3	. . .	. . . .	1000

perature and temperature differences for every 100 microvolts. Cold junction at 0°. particular element at some of the following fixed points:

Ag.	m. p.	960.2°	9111 μv
Au.	m. p.	1062.6°	10296 μv
Cu.	m. p.	1082.8°	10534 μv
Li_2SiO_3.	m. p.	1201°	11941 μv
Diopside.	m. p.	1391.5°	14230 μv
Ni.	m. p.	1452.6°	14973 μv
Pd.	m. p.	1549.5°	16144 μv
Pt.	m. p.	1755°	18608 μv

less except at the lower end of the scale. Similarly, in the list of fixed points given at the foot of Table II, the magnitude of the uncertainty in the temperature scale is such that the temperatures above 1000° may be rounded off to the nearest degree.

The reference curves given in Tables I and II are intended for use in conjunction with the appropriate deviation curve. This correction curve is determined for each element by calibration at several of the fixed points —preferably three or more—given at the foot of each table; whence it is simply constructed by plotting[1] $\Delta\mathbf{E}$ as ordinate ($\Delta\mathbf{E} = \mathbf{E}$ observed — $\mathbf{E}$ standard) against $\mathbf{E}_{\mathrm{obs}}$ as abscissa, and joining up the various points. Then in order to obtain the temperatures corresponding to the electromotive force reading indicated by the element, the appropriate value of $\Delta\mathbf{E}$ (as obtained from its deviation curve by inspection) is subtracted algebraically from the observed value of **E** before the latter is converted into degrees by means of the table. There need be no apprehension of error in the use of this method even with deviations of as much as 100 microvolts; especially if sufficient calibration points be taken within the specific temperature range, and if the deviation curve so obtained does not depart too far from a straight line.

It should be borne in mind that neither of these tables has an *absolute* significance; it represents merely an arbitrary reference curve which is substantially the mean of the three elements (E, F, G) used by Day and Sosman as standards; for the curve does not differ from the average reading of these elements by more than 1 microvolt, except at the somewhat less certain nickel point, where the divergence amounts to 5 microvolts.

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NOTE.

An Electrical Contact Vapor-Pressure Thermoregulator.—The change in the pressure of a saturated vapor with change in temperature has been made use of by various investigators as a means of automatic temperature control. Andreae[2] devised a thermoregulator in which a small quantity of some volatile liquid, such as ether, alcohol, or water, was utilized to increase the change of pressure per degree of a suitably enclosed volume of air or other gas. Lothar Meyer[3] made use of the same principle. Benoit[4] described a thermoregulator similar to the foregoing, with certain mechanical improvements. Kahlbaum[5] first devised a regulator depending only upon the vapor pressure of a saturated vapor, without the additional pressure of air or other gas. In all of the above devices the change of vapor pressure, or combined air and vapor pressure, regulated the rate of flow of the gas used in heating the air or water bath.

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[1] It is obvious that the required accuracy is secured by plotting on a small scale; a sheet of coördinate paper 20 × 20 cm. is ample.

[2] *Wied. Annalen*, 4, 614.

[3] *Ber.*, 16, 1088 (1883).

[4] *Wied. Beibl.*, 4, 296.

[5] *Ber.*, 19, 2860 (1886).

Recently Esclangon[1] has described a saturated vapor thermoregulator in which the increase in vapor pressure with temperature rise causes a movement of mercury in a circular tube, pivoted so as to rotate about its center. This movement of mercury destroys the equilibrium of the balanced system by displacing its center of gravity, causing the tube to rotate sufficiently to make and break an external electrical contact. This apparatus is obviously unsuited for the temperature control of a water bath in which the water is being vigorously stirred.

The form of vapor-pressure thermoregulator herein described is essentially an upright U-tube closed at both extremities. One side of the tube contains a volatile liquid whose boiling point lies near the desired temperature of the bath. Above the liquid is its saturated vapor with or without admixture of air or other gas. The pressure exerted by the vapor, or the vapor and gas, supports a mercury column, which makes and breaks an electrical contact on the other side of the U-tube. This contact is made in an atmosphere of carbon dioxide.

The use of air, in addition to the saturated vapor, influences the accuracy of the thermoregulator in several ways. (1) It augments by approximately one-tenth the pressure-increase per degree rise in temperature, when the air has atmospheric density. (2) It decreases the rate of evaporation of the liquid due to a temperature rise. (3) It increases both the specific heat and the thermal conductivity, two effects which tend to neutralize each other. The author has not attempted to investigate those conditions which correspond to a maximum pressure-increase per degree change in the temperature of the bath per second. However, it is probable that the use of a gas in addition to the saturated vapor increases slightly the sensitiveness of the apparatus.

An electrical contact thermoregulator, utilizing the pressure of saturated ether vapor, has been in use for some time in this laboratory. It has kept the temperature of a water bath of 350 liters capacity at 30° with an accuracy of from 0.01° to 0.005° for several days at a time, the room temperature being subject to the usual variations of the average laboratory. The bath is made of galvanized sheet iron, surrounded by 1-inch pine boards. During the warm weather no cover was used for the bath. During the colder weather, a cover of plate glass, in three pieces for convenience in handling, has been used. The heat is supplied by ordinary carbon filament incandescent lamps, and the bath is stirred by a 1/30 horse-power motor. The resistance in series with the motor consists of two 100 watt lamps in parallel, and these are dipped into the bath. Thus this source of heat is utilized. Two dry batteries operate the heating circuit through the thermoregulator and a 150 ohm relay. The inside dimensions of the bath are: depth, 70 cm.; width, 70 cm.; length, 80 cm.

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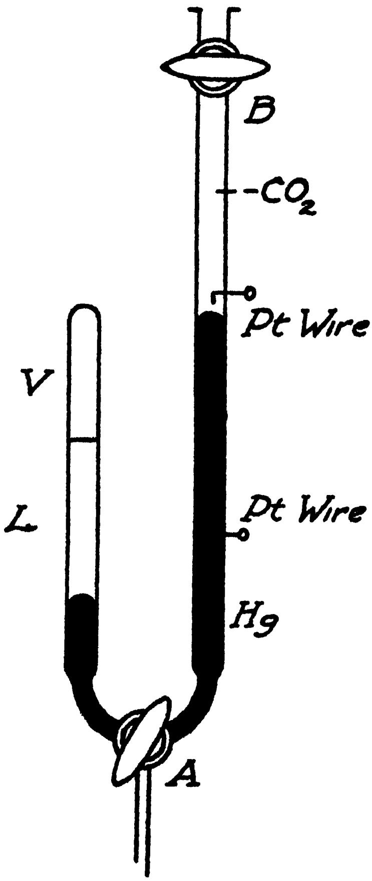
[1] *Compt. rend.*, 156, 1667–70 (1913).

In all cases where there has been a noticeable variation of temperature beyond the limits above mentioned, it has been due to failure of the relay to operate, caused by the contacts partially fusing together, or else to an insufficient heat supply, following a sudden drop in external temperature. As is usually the custom, a certain number of lamps are shunted around the relay so as to provide a constant amount of heat sufficient to keep the water bath near to the desired temperature. The remainder of the lamps operate through the relay and provide a variable amount of heat, depending on the external fluctuations of temperature.



Scale 1:3

When no cover is used, and when the room temperature varied between 27° and 30°, one 60 watt lamp has been found to furnish sufficient heat, in addition to the lamps used as resistance for the motor. When a cover is used, and when the room temperature varies between 18° and 23°, one 100 watt lamp and one 60 watt lamp are necessary, besides the motor-resistance lamps. In the latter case, the 100 watt lamp can be shunted around the relay. These specifications are only approximate, but will serve to give some idea of the heat requirement of the bath described above.[1]

The thermoregulator, as actually constructed, is shown in the accompanying figure. L is the liquid, above which is the saturated vapor; A is a three-way stopcock; B is a stopcock. As can be seen at once, air is here used in addition to the saturated ether vapor, the partial pressure of the former amounting to about

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[1] The author, since the preparation of this article, has reduced the heat requirement about 50% by the use of double-walls for the bath. The 1-inch space between the walls is filled with sawdust.

28 cm. of mercury at 30°. The pressure of the saturated ether vapor at 30° amounts to 63.6 cm. The carbon dioxide present in the other arm of the apparatus is at approximately atmospheric pressure.

To prepare for operation, the apparatus is first carefully cleaned and dried. It is then inverted, and pure, dry ether, or other liquid, is poured, by means of the lower outlet tube, into the proper arm until it contains several cc. Air is expelled at this time, if so desired, by gently warming the liquid. A is then turned until connection is made with the other arm of the U-tube; B is closed. Mercury, carefully freed from all impurities, including moisture, is poured into this side of the U-tube until nearly full. A is then turned so as to close both arms of the apparatus, which is then placed upright, as in the figure. B is opened. Connection is made between the two sides of the thermoregulator, after which B is again closed, preparatory to immersion in the water bath. Before it is placed in the bath, however, both stopcocks are protected by an application of buret wax, to guard against entrance of water vapor. In addition, the tube above B is closed by a rubber stopper, while the lower outlet tube is closed by a rubber tube and pinchcock.

The thermoregulator is now placed in the water bath, which is at the desired temperature. If the mercury column stands above the upper platinum contact, it is drawn off by means of the lower outlet tube. If it falls below this point, more mercury is added from the top. By such manipulation, the column of mercury can be easily adjusted so as to make and break contact at the desired temperature. Finally, the air above the platinum contact is replaced by dry carbon dioxide, a mercury seal placed above B, and the thermoregulator securely fixed in the water bath.

The vapor-pressure thermoregulator is surpassed in ultimate sensitiveness by the well-known toluene thermoregulator. That is, by using a large volume of toluene and causing it to expand in a tube of small diameter, we can theoretically increase the sensitiveness to any desired degree. It is impractical, however, to use a tube of a diameter much less than 2 mm., since in a smaller tube the mercury is apt to stick to the sides. An increase in the amount of toluene used causes the temperature of the toluene to lag considerably behind the temperature of the bath, especially where this is subjected to the influence of a considerable change of external temperature. This difficulty has been overcome, in part, by various workers by enclosing the toluene in long cylindrical tubes, placed around the walls of the thermostat.

The author has not actually compared the sensitiveness of the vapor pressure thermoregulator with that of the toluene thermoregulator, but one experiment will illustrate the rapidity with which the former can adapt itself to the changing temperature of a water bath.

The thermoregulator, adjusted to 30°, was removed from the bath and allowed to attain the room temperature of 25°. The water bath was then heated to 30.1°. The regulator, which had a temperature of 25°, was then immersed in the bath. In 30 seconds from the time of immersion, the thermoregulator automatically operated the relay and cut off the heating current. It is this rapidity of accommodation which makes the vapor-pressure thermoregulator especially suited for temperature control in those cases where no great care is taken to prevent any sudden change of external temperature and where the amount of heat, supplied under the control of the relay and thermoregulator, is in considerable excess of the exact amount required to maintain the bath at the desired temperature.

A gas thermoregulator so constructed as to be independent of atmospheric pressure would have, at room temperature, a maximum sensitiveness of approximately one-tenth that of the saturated ether vapor thermoregulator. This is true when the gas used exerts a pressure of 760 mm. at 0°. Of course, if it were possible to construct a thermoregulator containing a gas under high pressure, a degree of sensitiveness heretofore unattained could be secured. Referring to the PV isothermals of a gas, we see that the vertical distance between two consecutive isothermals, which represents the increase in pressure per degree at constant volume, can be made as large as desired by choosing high pressures and small volumes. The difficulty here, however, and it seems insurmountable, would be to devise a means of confining the gas at such high pressure without the use of a mercury column of huge dimensions.

Summary.

1. The author has devised a form of vapor-pressure thermoregulator unaffected by changes in atmospheric pressure, and utilizing an electrical contact in dry carbon dioxide gas.

2. The thermoregulator is light and easily adjusted, is adapted for use in fluid baths, and is unaffected by motion of the fluid.

3. The rapidity, with which it adjusts itself to changes in the temperature of the bath, makes it especially suitable for the accurate temperature control of the average thermostat.

4. It has an observed sensitiveness of 0.01° to 0.005°.

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INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES.

The third session of the Council of the International Association of Chemical Societies was held at the Institute Solvay, Brussels, September 19–23, 1913. The meeting was held in Brussels instead of London in acknowledgment of Monsieur Solvay's munificent, unconditioned gift of

Frs. 250,000 to the Association and also because of his bequest founding an International Institute of Chemistry with an endowment of Frs. 1,000,000.

The most important action taken by the Council was as follows:

After discussion of a report by Professor Werner on the investigation of the language difficulty in scientific literature, the committee was requested to report next year on three points:

(1) The Publication of an International Journal of Abstracts in three languages.

(2) The publication of three editions of an International Journal of Abstracts, *viz.*, in English, French, and German.

(3) The publication of an International Journal containing translations in either English, French or German of original papers appearing in the lesser known languages.

Professor Guye reported for the Commission on Abbreviations of the Titles of Scientific Journals and resolutions were adopted looking toward the adoption, if possible, of a uniform set of abbreviations on the basis of the "International Catalogue of Scientific Literature."

The following report of the International Commission for the Unification of Physico-Chemical Symbols was adopted.

In drawing up the list of symbols, the Commission decided to adopt, *as far as possible*, as a basis of notation, the following two principles, namely:

1. Each symbol shall have only one definite signification.
2. Where it appears impossible to avoid using the same letter for different quantities, the symbols shall be distinguished by a letter, added as subscript.

This second principle was also adopted in the case of individual members of a group, *e. g.*, volume, specific volume, molecular volume, critical volume, etc. The Commission, however, recognized that there are practical difficulties in the way of a strict adherence to these principles. Although, therefore, in the list of symbols recommended by the Commission, a given symbol may have more than one signification, the Commission have also suggested alternative symbols which may be used in those cases where confusion may arise. Thus, for example, the Commission recommends that R should be used as the symbol both for the gas constant and for electrical resistance; but that in those cases where there is a possibility of confusion, the alternative symbol R_w may be employed for the latter quantity. The addition of the letter W here recalls the use of this letter for electrical resistance frequently met with in Germany.

In making these suggestions, the Commission took into consideration the symbols proposed by the National Committees of the American, French, and London Chemical Societies, as well as by the Bunsen Gesellschaft, the Ausschuss für Einheiten und Formelzeichen, and the International Electrotechnical Commission. A large measure of agreement already existed between the proposals of these different bodies, but in those cases where there was disagreement, the reasons for the adoption by the Commission of the symbols recommended are stated in the column headed "Remarks."

The Commission decided to recommend the employment of only Greek and Roman characters, and, in the case of the latter, that the letters should be printed in the *italicized* (*sloping*) *form*. The Commission was of opinion that small Roman capitals should not be employed on account of the difficulty of distinguishing them from the ordinary letters.

	Symbols recommended.		
Name of quantity.	Usual symbol.	Alternative symbol to be used in cases where confusion with other symbols may arise.	Remarks.
1. General Physics and Mathematics.			
Acceleration due to gravity	g		
Ångström unit (10^{-10} metre)	*Å*		
Area	q		The symbols α, F, and s have been variously suggested. The Commission recommends q (quadrate, Quadrat), as a suitable international symbol.
Base of natural logarithms	e		
Co-ordinates, variables	x, y, z		
Critical quantities: pressure, volume, temperature (Centigrade), temperature (absolute), density	p_c v_c t_c T_c d_c		Recommended in place of Greek letters, in accordance with the general principles adopted by the Commission.
Density (mass per unit volume)	d	D	D may be used, for example, in the differential dD/dt.
Diameter	d		Suggested; not definitely recommended.
Differential sign, total	d		
Differential sign, partial	∂		
Fluidity	ϕ		Suggested; not definitely recommended.
Force	f		
Gas constant per mole	R		
Height	h		Suggested; not definitely recommended.
Increment	Δ		
Length	l		
Mass	m		
Mean free path	λ	λ_f	λ_f may be used in order to distinguish from λ = wave length of light.

Name of quantity.	Symbols recommended.		Remarks.
	Usual symbol.	Alternative symbol.	
1. General Physics and Mathematics—contd.			
Micron (10^{-6} metre)	μ		
Millimicron (10^{-9} metre)	$\mu\mu$		The Commission recognizes that the symbol $\mu\mu$ ($= \mu \times 10^{-3}$) is not strictly logical, but recommends that owing to the universality of its use it should be retained.
Number (of terms, revolutions, etc.); number of molecules	n		
Number of moles	N		
Pressure	p		
Pressure, osmotic	P		
Radius	r		
Ratio of circumference to diameter	π		
Reduced quantities: pressure, volume, temperature, density	p_r v_r T_r d_r		
Summation sign	Σ		
Surface tension	γ	σ	The use of γ is recommended as chief symbol on account of its employment in the classical researches dealing with this subject.
Time	t		
van der Waals' constants	a, b		
Variation sign	δ		
Velocity	u		
Velocity, angular	ω		
Velocity components in three directions	u, v, w		
Viscosity	η		This symbol is recommended as being in accordance with the usage among physicists.
Volume (in general)	v		
Volume, specific	v_s		
Volume, atomic	v_a		
Volume, molecular	v_m		
Weight, as gravitational force	w		
Work	W*		
2. General Chemistry.			
Atomic weight, and gram-atomic weight	A		
Concentration (units not specified)	C		
Equilibrium constant	K		

* The letter A has been adopted as the symbol for "Work" by the Ausschuss für Einheiten und Formelzeichen and by the International Electrotechnical Commission. The latter body has adopted W as an alternative symbol.

	Symbols recommended.		
Name of quantity.	Usual symbol.	Alternative symbol.	Remarks.
2. General Chemistry—contd.			
Mole fraction	x		
Molecular and gram-molecular weight	M		
van't Hoff coefficient	i		
Velocity coefficient	k		
3. Heat and Thermodynamics.			
Energy, in general	E		Suggested; not definitely recommended.
Entropy	Φ		This symbol, used by Willard Gibbs and others, is recommended, since S is adopted for molecular heat.
Intrinsic energy	U		
Latent heat, per gram	l		
Latent heat, per mole	L		
Mechanical equivalent of heat	J		
Molecular heat	S		
Molecular heat at constant pressure	S_p		
Molecular heat at constant volume	S_v		
Quantity of heat	Q		
Ratio of specific heats ($=S_p/S_v$)	γ		This symbol is recommended in preference to κ as being in growing use among physicists.
Specific heat	s		The symbol s is recommended in place of c as being in growing use among physicists, and to avoid confusion with "concentration."
Specific heat at constant pressure	s_p		
Specific heat at constant volume	s_v		
Temperature, Centigrade	t or $t°$	θ	θ may be used when "temperature" and "time" occur in the same expression.
Temperature, absolute	T		
4. Optics.			
Intensity of illumination	I	I_L	
Refractive index	n	n_r	Recommended as finding most general approval.
Refractive power, specific (Gladstone and Dale)	r_G $[r_G]_D^{t°}$		The second symbol is used when it is desired to indicate the temperature and wave length of light.
Refractive power, specific (Lorentz and Lorenz)	$\left\{\begin{array}{l} r_L \\ [r_L]_D^{t°} \end{array}\right.$		
Refractive power, molecular	$\left\{\begin{array}{l} R_G\ R_L \\ [R_G]_D^{t°}\ \ [R_L]_D^{t°} \end{array}\right.$		

Name of quantity.	Symbols recommended.		Remarks.
	Usual symbol.	Alternative symbol.	
	4. Optics—contd.		
Rotation, angle of optical........	α		
Rotatory power, specific..........	$[\alpha]$		
Rotatory power, molecular.......	$M[\alpha]$		Suggested; not definitely recommended.
Velocity of light.................	v		Suggested; not definitely recommended.
Wave length of light......	λ		
	5. Electricity and Magnetism.		
Capacity (electric)...............	C		
Charge, unitary (charge on an electron)	e		
Conductivity (specific conductance)	κ		
Conductivity equivalent..........	Λ		$\Lambda = 1000\kappa/$concentration in gram-equivalents per liter.
Conductivity equivalent (at different dilutions—volumes in liters containing 1 gram equivalent)	Λ_{10} Λ_v Λ_∞		
Conductivity, equivalent, of cation and anion	Λ_c Λ_A		
Conductivity, equivalent, of specified ions	$\Lambda_{K^{\cdot}}$ $\Lambda_{Cl'}$		
Current.........................	I		
Dielectric constant..............	K		As an *abbreviation*, the symbol *D.C.* is recommended.
Dissociation, electrolytic, degree of (degree of ionization)	α		This is recommended in preference to γ on account of the adoption of the latter symbol for surface tension and ratio of specific heats.
Electromotive force	E		
Faraday's constant............., .	F		
Permeability, magnetic...........	μ	μ_p	
Potential, single electrode, or decompositon potential of anion	$\epsilon_{K^{\cdot}}$, $_{Cl'}$		The symbol ϵ is recommended in place of E as the latter is adopted as the symbol for electromotive force.
Potential measured against the hydrogen or calomel electrode, respectively, which is taken as unity	ϵ_h, ϵ_c		
Quantity of electricity...........	Q		
Resistance......................	R	R_w	The symbol R has been adopted by the International Electrotechnical Commission.
Susceptibility, magnetic..........	κ		
Transport number of cation and of anion	n_C, n_A		

Name of quantity.	Symbols recommended.		Remarks.
	Usual symbol.	Alternative symbol.	
5. Electricity and Magnetism—contd.			
Velocity of cation and of anion in cm./sec. when the potential gradient is 1 volt/cm.	$U_C\ U_A$		
Velocity of specified ions under unit potential gradient	$U_{K^{\cdot}}\ U_{Cl'}$		

The Commission reserved consideration of symbols for the following quantities: Coefficient of self-induction; Concentration, expressed in various units; Current density; Diffusion coefficients; Free energy; Mobility of ions; Solubility; Critical solution temperature.

ALEX. FINDLAY, *Secretary.*

The Committee on Inorganic Nomenclature made the following report, which was adopted:

This Committee is unanimously in favor of adopting the symbols:

I for Iodine; Xe for Xenon; W for Wolfram; Nb for Niobium, but is of the opinion that the question of adopting the symbol Be for Beryllium, in place of Gl, should be referred to the prospective International Commission on Inorganic Nomenclature, with a strong recommendation in favor of the symbol Be.

The Committee recommends that in indexing inorganic compounds the constituent atoms, including carbon, should be arranged in alphabetical order.

It is not desirable to place carbon at the commencement of the formula as is usual in indexing organic compounds. It is, however, desirable to make an exception to the alphabetical order in the cases of hydrogen and oxygen, which should always be placed at the end of the formula.

In order to facilitate reference to compounds containing water of crystallization, it is suggested that it would be desirable to insert, after the formula of the anhydrous compound, the formulae of the hydrated varieties, both in the form $F + xH_2O$, and in the empirical form with the hydrogen and oxygen embodied therein.

Binary compounds are to be regarded as additive and not as substitution compounds, the negative component forming the termination, and indicating the class of compound, and the positive component providing the name of the individual.

The recommendations of the Austrian and Russian National Committees for indicating the relative numbers of atoms of each element in the molecule are approved; *e. g.*, N_2O_5 becomes dinitrogen pentoxide and not nitrogen pentoxide.

In order to obtain shorter names for substances, it is considered desirable to indicate the valency of the positive component by means of a suffix, the valencies one to eight being represented by the suffixes o, a, i, e, -on, -an, -in, -en, in the order given, *e. g.*, the two chlorides of mercury would be respectively named mercuro and mercura chloride.

It is recommended that an International Commission composed of one member from each country represented in the Association, be appointed, with Professor Werner as chairman, by November 1, 1913, at latest.

This International Commission should appoint a small working Committee of seven members, whose expenses should be defrayed out of the funds of the International Association of Chemical Societies.

The Committee on Organic Nomenclature recommended the appointment of a small working committee of five members, not necessarily members of the Council, to receive and consider the reports of the National Committees and further to suggest methods for the organization and carrying out of future work, the expenses of the committee to be defrayed from the funds of the Association. This recommendation was adopted and similar action was taken with regard to further work on Inorganic Nomenclature and on the Unification of Physico-Chemical Symbols.

Societies Affiliated to the International Association of Chemical Societies with the Date of Entry into the Association.

In accordance with Article V of the Statutes, this list of the Societies is arranged in alphabetical order of the names, in the French language, of the countries they represent.

	Date of entry.	Number of members.
Deutsche Chemische Gesellschaft	April 25, 1911	3356
The Chemical Society (London)	April 25, 1911	3202
Verein Österreichischer Chemiker	October 28, 1911	1050
Société Chimique de Belgique	August 6, 1913	510
Kemisk Forening, Kjòbenhavn	January 23, 1912	155
Sociedad Española di Fisica y Quimica	April 10, 1912	353
American Chemical Society	October 6, 1911	6091
Société Chimique de France	April 25, 1911	1023
Nederlandsche Chemische Vereeniging	July 14, 1911	515
Società Chimica Italiana	January 11, 1912	654
Tokyo Chemical Society	March 18, 1912	567
Polyteknisk Forenings Kemikergruppe, Kristiania	October 27, 1911	125
Russian Chemical Society	October 22, 1911	410
Schweizerische Chemische Gesellschaft	August 3, 1911	367

The following Societies, not represented on the Council, each sent one delegate in an advisory capacity only to the meetings in Brussels, September, 1913.

Deutsche Bunsen Gesellschaft für Angewandte Physikalische Chemie	June 19, 1911	777
The Faraday Society (London)	April 30, 1912	202
Société de Chimie Physique	June 15, 1911	225
		19,582

Statutes were proposed for the affiliation of the International Committee on Atomic Weights with the International Council.

As the International Council of Chemical Societies now has funds of its own, the expenses of the meeting no longer fall on the individual societies forming the Association.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE INFLUENCE OF HYDROGEN ION AND OF NEUTRAL SALTS UPON COLOR CHANGES AND REACTION VELOCITIES AMONG DYES OF THE TRIPHENYLMETHANE SERIES.

(ON CATALYSES WITH WEAK ACIDS, V.)

BY H. C. BIDDLE.

Received October 7, 1913.

1. Introductory.—As I have shown,[1] the speed of the assumption of color in the well-known magenta test for aldehydes, in the presence of excess of weak acids, closely resembles the conversion of the cinchona alkaloids into their toxins under like conditions. Thus the speed increases with acids of decreasing dissociation constant and decreases with acids of increasing dissociation constant. Furthermore the speed of the conversion increases in the presence of a weak acid, such as acetic, with the molecular concentration of the acid. Here, as in the case of the cinchona alkaloids, at least two factors apparently enter into the reaction—the inhibiting influence of the H^+ ion on the one hand and the accelerating influence of the molecule of the organic acid on the other.

The study of this catalysis was extended from the more complicated magenta reaction to the less involved conversion of a triphenylmethane dye from the colorless to the colored form, attention having been confined to the behavior of methyl violet in the presence of chloroacetic and acetic acids. Here, as in the case of the magenta reaction, the speed of conversion of the benzenoid to the quinoid form, in the approach toward a condition of equilibrium between the two forms, was found to be greater in the presence of the acid of lower dissociation constant. Subsequent study has shown that this law is general in its application to similar dyes of the triphenylmethane series, the reaction rate being a function, as will appear later, of the diminishing concentration of the H^+ ion. Thus, for example, rosaniline, para-rosaniline, malachite green and methyl violet all exhibit the same general phenomenon with normal solutions of such acids as chloroacetic, acetic, propionic etc., the speed of the reaction increasing with acids of decreasing dissociation constant.

In the previous paper on this catalysis[2] the question was raised, as to whether the speed of this reaction is a function *solely* of the diminishing concentration of the H^+ ion, or whether, as is the case in the conversion of the cinchona alkaloids into their toxins, it is dependent also upon the nature of the acid employed. The experimental results lead to the former conclusion. In the catalysis of the rosaniline dyes as in that of the cinchona alkaloids, the speed of the reaction is conditioned upon the diminishing concentration of the H^+ ion,[1] but unlike the latter case it is not a function of the molecular concentration of the organic acid.[2] In the case of the dye, indeed, the speed of the conversion from the benzenoid to the quinoid form not only does not increase with increasing concentration of acid, but actually decreases under such conditions.

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[1] THIS JOURNAL, 35, 273 (1913).

[2] Biddle, THIS JOURNAL, 35, 281 (1913).

Furthermore, while in the case of the cinchona alkaloids diminution of the H^+ ion through addition to an organic acid of a salt with a common acid ion exerted but a slight effect,[3] such an addition in the case of the color change enormously accelerates the speed of the reaction.

Variations in the concentration of the H^+ ion are found to produce not only an alteration in the speed of the reaction, but also an alteration in depth of color and in some cases a complete shift in color tint. The effect of such variations, in other words, is both static and dynamic. These variations in color tint correspond with the observations already made by Szyszkowski[4] and others in the case of certain dyes.

Not less interesting is the "neutral salt effect" in the presence of highly dissociated acids. Results are obtained here strictly comparable with those investigated by Arrhenius,[5] Euler,[6] Spohr,[7] Stieglitz,[8] Acree,[9] Kellogg[10] and others in the case of the inversion of cane sugar, hydrolysis of esters and similar reactions. In other words, the addition of foreign salts to solutions of equal concentration of acid produces an effect equivalent to that of increasing the concentration of the H^+ ion. In the case of the inversion of cane sugar and the hydrolysis of esters, this leads to only one result—an increase in the speed of the reaction. In the case of the rosaniline dyes, however, such addition produces, as does variation of the H^+ ion, a static as well as a dynamic effect.

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[1] This conclusion is fully in accord with the careful research of Sidgwick and his coworkers, which unfortunately I had until recently overlooked. In their investigations of reaction velocities in the case of brilliant green, malachite green and diamino triphenylcarbinol in the presence of acids and alkalies, they call attention, in the action of acid upon the carbinol base, to the diminishing speed of the reaction with increasing concentration of acid, but they are unable to account for the phenomenon (Sidgwick and Moore, *Z. physik. Chem.*, 58, 385 (1907); *J. Chem. Soc.*, 95, 889 (1909) Sidgwick and Rivett, *Ibid.*, 95, 899 (1909)).

[2] Biddle, *Ber.*, 45, 2837 (1912). Biddle and Rosenstein, THIS JOURNAL, 35, 425 (1913).

[3] Biddle and Rosenstein, THIS JOURNAL, 35, 425 (1913).

[4] *Z. physik. Chem.*, 58, 420 (1907).

[5] *Ibid.*, 1, 110 (1881); 4, 237 (1889); 31, 197 (1899).

[6] *Ibid.*, 32, 348 (1900).

[7] *J. prakt. Chem.*, [2] 33, 270 (1886).

[8] *Am. Chem. J.*, 32, 224 (1904); 34, 1689 (1905); 39, 177, 596, 720 (1908); THIS JOURNAL, 34, 1689 (1912).

[9] *Am. Chem. J.*, 38, 259, 489 (1907); 39, 226 (1908); 41, 474 (1909).

[10] THIS JOURNAL, 31, 403, 886, 889 (1909); 35, 396 (1913).

The static effect of the H^+ ion and of neutral salts upon phenolphthalein has been made the subject of careful study by Rosenstein[1] in his investigation of the ionization constant of the indicator.

2. The Speed of the Reaction, a Function of the Diminishing Concentration of the H^+ Ion.—As we have noted in the case of the cinchona alkaloids, both the nature of the acid and the concentration of the H^+ ion functionate in the catalysis to the toxins. In the color change of the triphenylmethane dyes, on the contrary, the speed of the reaction is a function of the diminishing concentration of the H^+ ion *without regard to the nature of the acid.* This is clearly shown in comparing the behavior of these dyes in the presence of acids of widely different nature, such as acetic and hydrochloric acids. In isohydric solution of the two acids, the dye exhibits the same color tint.

The alteration in tint and color with varying concentration of H^+ ion is very noticeable in the case of methyl violet, where, with diminishing concentration of hydrochloric acid, the color will shift from yellow through green, blue, blue-violet to rose-violet. Since isohydric solutions of different acids effect the same color change, one is led to suspect that the speed of the assumption of color, in the conversion of the carbinol base to the quinoid dye, will be found to be intimately associated with the diminishing concentration of the H^+ ion, and will be at the same time largely independent of the nature of the acid employed. This probability is fully confirmed by experiment. In isohydric solutions of hydrochloric and acetic acids, indeed, the speed of the conversion of the colorless into the colored form of the dye, in approaching the condition of equilibrium, is *identical.* The speed of the catalysis,[2] consequently, differs from that of the cinchona alkaloids in that it is independent of the *nature* of the particular acid employed.

3. The Relation of the Speed to the Diminishing Concentration of the H^+ Ion.—In the tables given below are presented the data representing the relation between speed of transformation and concentration of the H^+

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[1] Rosenstein, THIS JOURNAL, 34, 1117 (1912).

[2] If, according to the suggestion of Ostwald, the term catalysis is employed to signify the acceleration or retardation of a chemical reaction by substances which themselves undergo no permanent change as a result of their reaction, a question may be raised as to the legitimacy of using the term in this case, since in this reaction, without doubt, H^+ ion enters into the reaction in the formation of ions of a mono-, di- and triacid base. In the light, however, of other phenomena which will be considered in a later paper, it seems well for the present to employ the term in the consideration of this reaction.

ion in the case of methyl violet, in the presence of hydrochloric acid of varying concentration. The method of procedure in the experimental determination, which, with slight modifications as to amounts, applies equally well to rosaniline, pararosaniline, or malachite green, was as follows:

A standard solution of the carbinol base was prepared by adding to a mixture of 200 cc. of water and 200 cc. of absolute alcohol, 20 cc. of a 0.1% solution of methyl violet and to this in turn sufficient caustic potash to produce complete decolorization of the solution on standing (14 cc. of a 0.5 *N* KOH solution were used). The color standard was prepared, in the case of each strength of acid, by adding from a buret 10 cc. of the carbinol solution to 50 cc. of the acid, the resulting solution being permitted to stand in each case until equilibrium color had been reached. In each solution prepared for testing, exactly 2 cc. of the carbinol base were added to 10 cc. of acid, care being taken to thoroughly agitate the acid during the addition. The alkali content of the standard carbinol solution was determined by titration[1] and the acid neutralized by the base contained in the 2 cc. of this solution was deducted in each case from the acid present. The free acid is assumed in each case to be completely dissociated and to occupy the actual volume resulting from the addition of the carbinol base (2 cc.) to the acid (10 cc.), or 12 cc. in all. If the methyl violet base is regarded as pentamethyltriaminotriphenylcarbinol, its concentration in the final solution is approximately 0.00002 molal. The measurements were made as before[2] at 19.5°(±0.2°) in a Stammer colorimeter, the tube containing the solution studied being 50 mm. in length. Each reading is, in general, the mean obtained from two successive determinations.

Although the colorimetric method does not lend itself to high accuracy of measurement, the results obtained are sufficiently definite to give us clear information regarding the influence of the H^+ ion. The speed of the reaction, while diminishing slightly in some cases with successive intervals of time, is apparently that of a reaction of the first order with respect to the color base.

Consequently:

$$dx/dt = K(a - x).$$

Integrating:

$$K_1 = 1/t \log a/a - x,$$

or

$$K_2 = 1/t_2 - t_1 \log a - x_1/a - x_2.$$

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[1] The base in the carbinol solution was determined by adding phenolphthalein to a measured volume and titrating with 0.005 *N* HCl until color had just disappeared. With care, a colorless end point is obtained which does not show the color of methyl violet until after the lapse of a short time.

[2] Biddle, THIS JOURNAL, 35, 279 (1913).

TABLE I.

Concentration of free hydrochloric acid.................. 0.0375 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0	0.0	50.0	...	...
5	5.4	44.6	0.00993	0.00993
10	9.4	40.6	0.00904	0.00816
15	13.3	36.7	0.00895	0.00877
20	16.5	33.5	0.00869	0.00792
25	19.6	30.4	0.00864	0.00843
		Mean,	0.00905	0.00864

TABLE II.

Concentration of free hydrochloric acid.................. 0.0055 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0	0.0	50.0	...	...
5	7.4	42.6	0.01391	0.01391
10	13.3	36.7	0.01343	0.01295
15	17.7	32.3	0.01265	0.01109
20	21.5	28.5	0.01221	0.01087
25	24.9	25.1	0.01197	0.01103
		Mean,	0.01283	0.01197

TABLE III.

Concentration of free hydrochloric acid.................. 0.0033 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0	0.0	50.0	...	...
5	8.5	41.5	0.01618	0.01618
10	14.9	35.1	0.01536	0.01455
15	20.7	29.3	0.01547	0.01569
20	24.9	25.1	0.01497	0.01344
		Mean,	0.01549	0.01496

TABLE IV.

Concentration of free hydrochloric acid.................. 0.00216 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0	0.0	50.0	...	...
2	7.3	42.7	0.03427	0.03427
4	12.9	37.1	0.03239	0.03053
6	17.8	32.2	0.03185	0.03076
8	21.9	28.1	0.03128	0.02957
10	25.5	24.5	0.03098	0.02977
		Mean,	0.03215	0.03098

TABLE V.

Concentration of free hydrochloric acid.................. 0.00155 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K_1.	K_2.
0...........	0.0	50.0	...	...
2...........	11.2	38.8	0.05507	0.05507
4...........	19.3	30.7	0.05296	0.05085
6...........	25.7	24.3	0.05228	0.05077
8...........	30.8	19.2	0.05195	0.05115
10...........	34.5	15.5	0.05086	0.04648
			Mean, 0.05262	0.05086

TABLE VI.

Concentration of free hydrochloric acid.................. 0.00095 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K_1.	K_2.
0............	0.0	50.0	...	...
1............	13.6	36.4	0 13787	0.13787
2......... ...	22.7	27.5	0.13140	0.12494
3............	28.9	21.1	0.12489	0.11188
4............	34.1	15.9	0.12439	0.12288
5............	37.5	12.5	0.12041	0.10448
6	40.7	9.3	0.12175	0.12843
			Mean, 0.12678	0.12175

TABLE VII.[1]

Concentration of free hydrochloric acid.................. 0.00034 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i e.*, *x*.	*a* — *x*.	K_1.	K_2.
0............	0.0	50.0	...	...
1............	40.0	10.0	0.69897	0.69897
2............	47.5	2.5	0.65052	0.60206
			Mean, 0.67474	0.65051

These experimental results are given in Figs. 1 and 2, the speeds, $K_1 \times 10^3$, being plotted as abscissas and the molal concentrations of the H^+ ion[2] $\times 10^4$ being plotted as ordinates. The graphs in the two figures are the same, that in Fig. 2 being on a scale sevenfold larger than that in Fig. 1.

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[1] The reaction is so rapid at this low concentration of H^+ ion that it is difficult to obtain accurate readings. The experimental error is consequently larger in this case than in the others.

[2] Since 0.0375 molal hydrochloric acid is dissociated to the extent of approximately 97.5%, the assumption of complete dissociation at this concentration introduces a negligible error in plotting the curve. In all the experiments the influence upon the ionization by the alcohol introduced from the methyl violet solution (about 1 vol. in 12 vol.) is ignored. It may be noted, however, that the ratio between the alcohol and the remainder of the solution is in all cases the same.

A consideration of this curve is of some interest. It shows very clearly that while the speed of the reaction in approaching the condition of equilibrium is a function of the diminishing concentration of the H^+ ion, it is not a *linear* function of that value. Between the limits of 3.75×10^{-2} and 5.5×10^{-3} molal concentration of H^+ ion, the speed[1] of the color change varies but slightly with varying concentration of the H^+ ion. Below the latter value the speed experiences a rapidly progressive increase until, at concentrations of the H^+ ion varying from 1.55×10^{-3} to 3.4×10^{-4} molal, the increments of speed with succeeding decrements in the concentration of the H^+ ion become enormous.

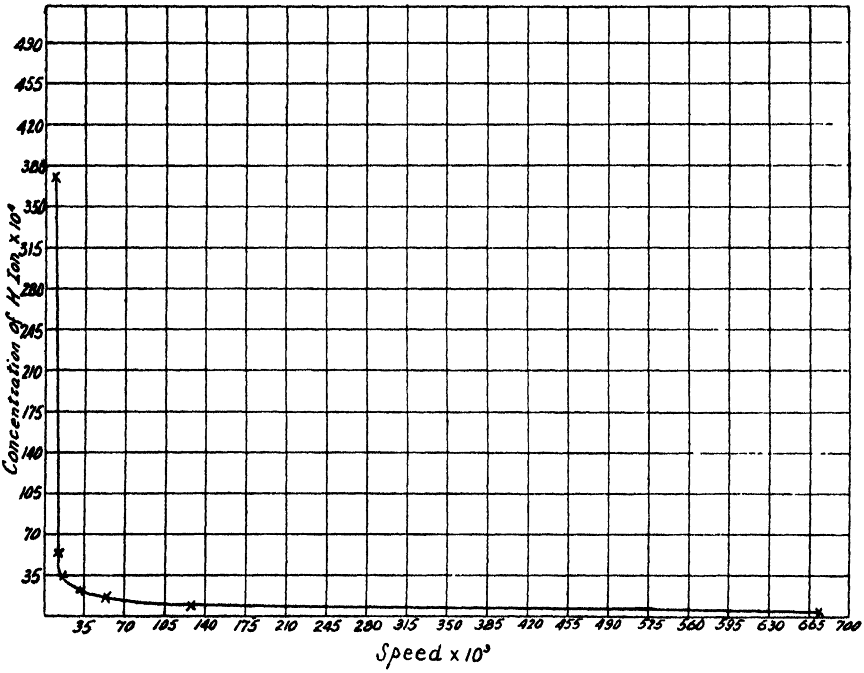

Fig. 1.

The complexity of this curve precludes the possibility of the speed of the reaction being expressed as any simple function of the concentration of the H^+ ion. Interestingly enough, however, the speed of the reaction appears to be a linear function of the square of the concentration of the OH^- ion. If, for example, the reciprocal of the concentration of the H^+ ion is represented by y and the values of $y^2 \times 10^{-4}$ are plotted as ordinates, while the speeds $\times 10^3$ are plotted as abscissas, the graph

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[1] It is to be noted that in comparing the speeds of approach to a condition of equilibrium in each case, we are not comparing the speeds of approach to a *common* depth of color. Since slight variations in concentration of the H^+ ion alter the color tint, it becomes impossible to make the latter comparison with any degree of accuracy. In general the color of the equilibrium color standard becomes lighter with increasing concentration of H^+ ion. The result is that if the speed values could be reduced to those of approach to a common depth of color, the variations in speed with varying concentration of H^+ ion would be somewhat greater than those observed, since the low values would then become lower and the high values higher.

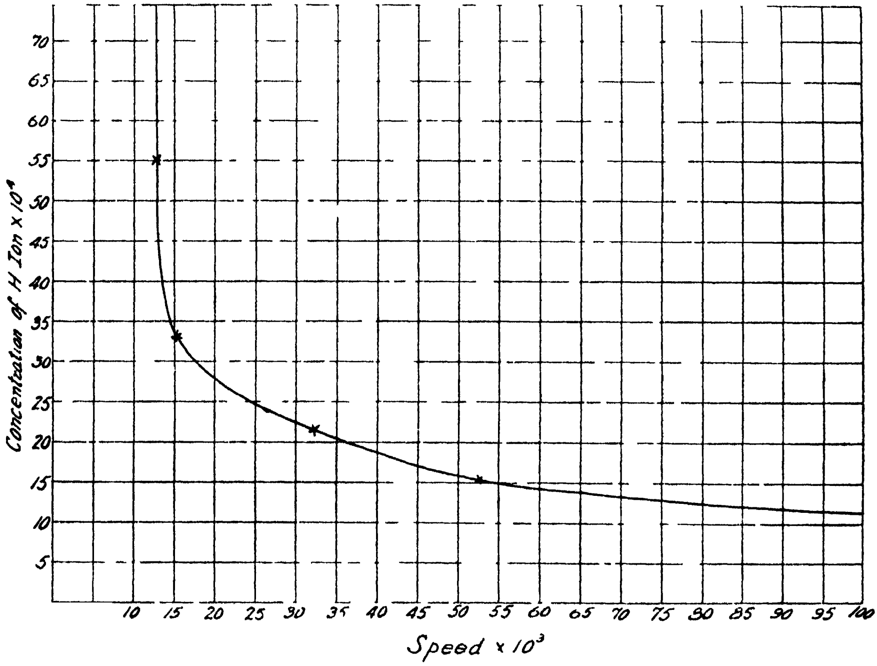

Fig 2.

given in Fig. 3 is obtained. Discarding the value taken from Table VII, because of the necessary inaccuracy of measurement in this case, the speed, within the limits of experimental error, appears to be a linear function of y^2.[1]

4. The Influence of Change of Temperature upon the Speed of the Reaction.—The speed of the conversion of the carbinol base into the quinoid dye varies to a considerable extent with changes in temperature, the speed in general increasing with rising temperature. Such an effect is in accord with the results obtained by Noyes[2] as to the decreasing dissociation of an acid with rise of temperature, but can scarcely be attributed solely to this cause.

The variations in speed with slight changes in temperature are found to be slight in the region in which alterations in the concentration of the H^+ ion produce little variation in the velocity of the reaction, but become very large in the region in which such variations are accompanied by marked changes in speed. Thus in concentrations of H^+ ion ranging from 3.75×10^{-2} to 5.5×10^{-3} molal a few degrees change of temperature produce but slight effect as compared with similar alterations within the range of concentration varying from 2×10^{-3} to 3.4×10^{-4} molal. A few degrees rise of temperature within the latter range increases the speed greatly. This is clearly shown in the following case with dilute hydrochloric acid, where a rise of roughly 4° increases the speed of the reaction almost 50%.[1]

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[1] In this connection I wish to thank Prof G N Lewis of this department for calling my attention to this interesting relation after he had considered the data given above.

[2] A. A. Noyes, THIS JOURNAL, 30, 346 (1908).

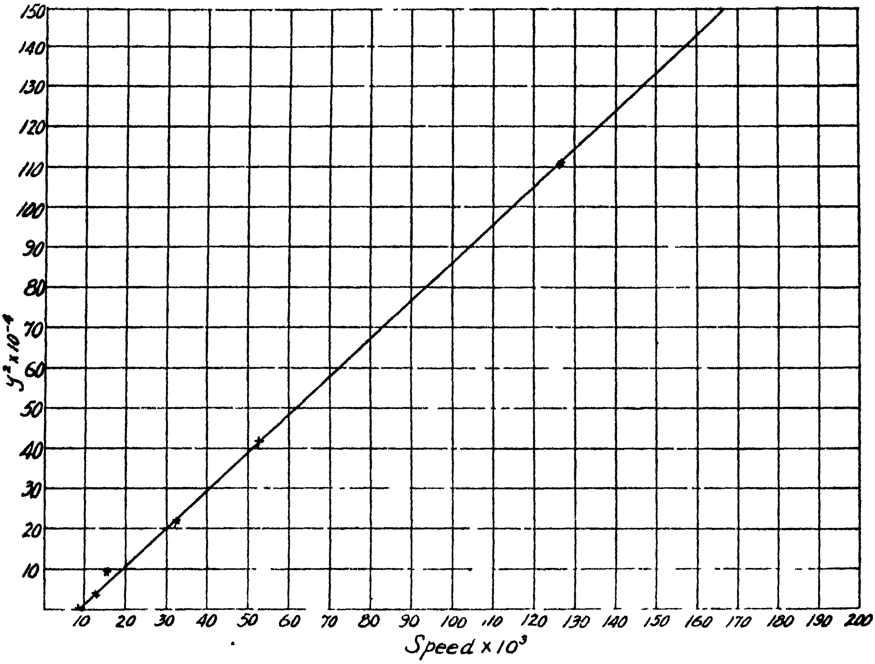

Fig. 3.

TABLE VIII.

Concentration of free hydrochloric acid .... 0.00176 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K_1.	K_2.
0	0.0	50.0	...	...
2	10.5	39.5	0.05118	0.05118
4	18.5	31.5	0.05017	0.04914
6	24.7	25.3	0.04931	0.04760
8	30.0	20.0	0.04974	0.05104
		Mean,	0.05010	0.04974

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[1] A careful study of this temperature effect is in progress in this laboratory.

TABLE IX.

Concentration of free hydrochloric acid.............. 0.00176 Molal.

Temperature.............................. 23.5°(±0.5°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K_1.	K_2
0	0.0	50.0	.	. .
2	15.0	35.0	0.07745	0.07745
4	24.6	25.4	0.07353	0.06962
5	28.5	21.5	0.07331	0.07240
6	32.0	18.0	0.07395	0.07716
		Mean,	0.07456	0.07415

5. Variations in Speed through the Addition of Salts.—The influence of the H^+ ion upon the speed of this catalysis naturally leads to a study of the effect of varying the concentration of this ion in solutions of uniform concentration with respect to the acid employed. Such variation is easily produced by the addition of suitable salts to the solution. Decrease in the concentration of the H^+ ion is of course readily effected in the case of a weak acid by the addition of a highly dissociating salt with a common acid ion, and, as Arrhenius[1] has shown, increase in the concentration of the H^+ ion is produced in the case of such an acid by the addition of soluble foreign salts, it being of course understood that the salt added in the latter case is not that of a weak acid. In the study of the cinchona alkaloids the addition of a salt with a common acid ion was found to exert at most a slight, if not an inappreciable effect upon the speed of the catalysis.[2]

From the large variation in speed already noted in the conversion of the carbinol form of a rosaniline dye into its quinoid form with slight variation in the concentration of the H^+ ion, we would naturally expect in this case that in the presence of weak acids large variation in speed would be brought about by the addition of suitable salts. The expectation is fully realized. Addition of a salt with a common acid ion, for example, greatly accelerates the speed of the conversion. To such an extent may this be increased, indeed, that it may become almost instantaneous. On the other hand, addition of a salt, such as sodium or potassium chloride, greatly retards the speed of the conversion. Sufficient addition, indeed, may almost if not altogether inhibit the change. It is thus possible in the solution of a weak acid, such as acetic acid, to effect through the addition of different salts a variation in the speed of the conversion ranging well-nigh from zero to infinity.

In the determinations which are recorded below the speed of the conversion was measured in the case of normal acetic acid and in the case of normal acetic acid containing on the one hand sodium acetate and on the other sodium chloride. The concentrations of acid and salt represent the actual concentrations after the addition to 10 cc. of solution of 2 cc. of the methyl violet. The acid neutralized by the alkali in the methyl violet and the minute quantity of salt formed therefrom are, however, in these cases ignored.

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[1] *Z. physik. Chem.*, 31, 197 (1899).

[2] Biddle and Rosenstein, THIS JOURNAL, 35, 425 (1913).

TABLE X.

Concentration of free acetic acid........................ 0.833 Molal.
Temperature.................................... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0...........	0.0	50.0	...	...
5...........	11.0	39.0	0.02158	0.02158
10...........	18.2	31.8	0.01965	0.01773
15...........	24.6	25.4	0.01832	0.01627
20...........	28.5	21.5	0.01833	0.01810
			Mean, 0.01947	0.01842

TABLE XI.

Concentration of free acetic acid....... .... 0.833 Molal.
Concentration of sodium acetate....... . . .. 0.00833 Molal.
Temperature.......... .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0............	0.0	50.0	...	...
1............	8.0	42.0	0.07572	0.07572
2............	12.9	37.1	0.06480	0.05388
3............	18.5	31.5	0.06689	0.07106
4............	22.4	27.6	0.06452	0.05740
5............	25.7	24.3	0.06267	0.05530
			Mean, 0.06692	0.06267

TABLE XII.

Concentration of free acetic acid........................ 0.833 Molal.
Concentration of sodium acetate........................ 0.0833 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0............	0.0	50.0	...	...
1............	32.0	18.0	0.44369	0.44369
2............	43.6	6.4	0.44639	0.44909
3............	47.7	2.3	0.44575	0.44445
			Mean, 0.44527	0.44574

TABLE XIII.

Concentration of free acetic acid.................... 0.833 Molal.
Concentration of sodium chloride.................... 0.0833 Molal.
Temperature.................................... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., i. e., x.	$a - x$.	K_1	K_2.
0	0.0	50.0	...	..
5	6.0	44.0	0.00910	0.00910
10	10.5	39.5	0.01023	0.00937
15	14.4	35.6	0.00984	0.00903
20	17.7	32.3	0.00948	0.00845
25	21.4	28.6	0.00970	0.01057
			Mean, 0.00967	0.00930

TABLE XIV.

Concentration of free acetic acid.................... 0.833 Molal
Concentration of sodium chloride.................... 0.416 Molal.
Temperature.................................... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., i. e., x.	$a - x$.	K_1.	K_2.
0	0.0	50.0	..	..
5	4.0	46.0	0.00724	0.00724
10	6.8	43.2	0.00635	0.00546
15	9.4	40.6	0.00603	0.00539
20	11.5	38.5	0.00567	0.00461
			Mean, 0.00632	0.00567

In the effect of neutral salts upon the speed of this catalysis it is of interest to raise the question as to whether or not the effect is due *entirely* to the varying concentration of the H^+ ion of the weak acid. In his research "Ueber die Änderung der Stärke schwacher Säuren durch Salzzusatz," in which he makes use of the speed of the inversion of cane sugar to determine the increase in the dissociation constant of a weak acid produced by the presence of a foreign salt, Arrhenius shows that the increase in the speed of the conversion is modified by two other conditions, *viz.*, (*a*) the formation of new electrolytes through double decomposition and (*b*) a direct effect of the neutral salt on the catalysis.[1]

In the conversion of the colorless form of a rosaniline dye into the colored form in the presence of a weak acid such as acetic acid and a salt of this acid such as sodium acetate, condition (*a*) could not arise, since no new electrolyte would be formed. In the retarding influence of a foreign salt, such as sodium chloride, however, new electrolytes would naturally be formed and (*a*) must be taken into consideration. In such a case the general effect as Arrhenius has shown would be to increase slightly the concentration of the H^+ ion.

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[1] *Z. physik. Chem.*, 31, 197 (1899).

The direct effect (*b*) of a neutral salt upon the catalysis must now be considered. This, *the "neutral salt effect" proper*, may be investigated by studying the influence of such a salt on the speed of the reaction in the presence of a dilute solution of a highly dissociated acid, such as hydrochloric acid.

As I have already pointed out (page 86) the color tint of the rosaniline dyes, such as rosaniline, malachite green and methyl violet, shifts with varying concentration of the H^+ ion. In the case of methyl violet this may lead to a complete change, the color in this case with increasing concentration of H^+ ion varying from rose-violet through blue to grass green and at higher concentrations to yellow. The general effect of increasing concentration of a chloride such as sodium chloride on a dilute solution of hydrochloric acid would naturally be to diminish somewhat the concentration of the H^+ ions. Under such conditions we should expect an alteration in color tint corresponding to such decrease. Interistengly enough, the color change is just the reverse. The alteration of color tint produced in a rosaniline dye in dilute hydrochloric acid by the addition of a chloride such as potassium, sodium or magnesium chloride is uniformly in the direction following an *increasing* concentration of the H^+ ion. Salts of similar highly dissociated acids such as the bromides and nitrates produce a similar effect, though not quite so pronounced in the case of the nitrates. Thus, in a 0.005 molal solution of hydrochloric acid, containing methyl violet of similar concentration to that used in the preceding experiments, increasing concentration of magnesium chloride will cause a variation of color from violet through blue to grass green, precisely as is effected by an increase in the concentration of the H^+ ion.

In view of these results it became of great interest to determine how the *speed* of the conversion of the colorless to the colored base would be affected under such conditions by the presence of a neutral salt. Direct measurements revealed the fact that the speed was indeed altered under such conditions, and that the alteration was in the same direction as that indicated by the shift of color tint. In other words, the presence of a chloride such as sodium chloride lessened the speed of the reaction. Furthermore, the speed of approach to a condition of equilibrium in the case of a given color tint was found to correspond with the speed observed in the case of the same color tint produced by definite increase in the concentration of hydrochloric acid. Thus, a solution containing 2 molal sodium chloride and 0.00176 hydrochloric acid showed less than $^1/_4$ the speed exhibited by the acid alone, giving an effect corresponding to an increase in the concentration of the H^+ ion of more than 200% and this in a solution of such dilution with respect to the acid, that the latter in the absence of the salt may be regarded as completely dissociated. These results are set forth in the following determinations:

TABLE XV

Concentration of free hydrochloric acid				0 00176 Molal
Temperature				19 5°(±0 2°)

Time Min	Depth of color in mm i e x	a − x	K1	K2
0	0 0	50 0		
2	10 5	39 5	0 05118	0 05118
4	18 5	31 5	0 05017	0 04914
6	24 7	25 3	0 04931	0 04760
8	30 0	20 0	0 04974	0 05104
			Mean, 0 05010	0 04974

TABLE XVI

Concentration of free hydrochloric acid				0 00176 Molal
Concentration of sodium chloride				0 0416 Molal
Temperature				19 5°(±0 2°)

Time Min	Depth of color in mm i e x	a — x	K1	K2
0	0 0	50 0		
2	7 5	42 5	0 03529	0 03529
4	13 5	36 5	0 03417	0 03305
6	19 0	31 0	0 03460	0 03546
8	23 5	26 5	0 03445	0 03405
			Mean, 0 03462	0 03446

TABLE XVII

Concentration of free hydrochloric acid				0 00176 Molal
Concentration of sodium chloride				0 416 Molal
Temperature				19 5°(±0 2°)

Time Min	Depth of color in mm i e, x	a — x	K1	K2
0	0 0	50 0		
5	8 6	41 4	0 01639	0 01639
10	15 5	34 5	0 01612	0 01584
15	20 4	29 6	0 01518	0 01331
20	25 0	25 0	0 01505	0 01467
			Mean, 0 01568	0 01505

TABLE XVIII

Concentration of free hydrochloric acid				0 00176 Molal
Concentration of sodium chloride				2 05 Molal
Temperature				19 5°(±0 2°)

Time Min	Depth of color in mm i e, x	a — x	K1	K2
0	0 0	50 0		
5	7 4	42 6	0 01391	0 01391
10	12 5	37 5	0 01249	0 01108
15	16 5	33 5	0 01160	0 00980
20	20 0	30 0	0 01110	0 00959
			Mean, 0.01225	0 01109

In general the action of a neutral salt was found to diminish with increasing concentration of acid. Thus while the influence of sodium chloride upon the color and the speed of the reaction in a 0.0375 *N* hydrochloric acid solution is of the same general character as in the case of the diluter acid, the effect is much less pronounced. This is fully in accord with the observation made by Arrhenius[1] in the catalysis of sugar, etc., that neutral salts act more strongly in the presence of dilute acids than in the presence of those of higher concentration.

The behavior of sulfates in this catalysis is of interest as it seems at first glance not to correspond with that of the salts of the monobasic acids. In other words, the retarding effect does not appear in the case of neutral sulfates. Thus, the reaction velocity in 0.00176 *N* hydrochloric acid, containing 0.416 molal magnesium sulfate, was found to be 0.05018, or practically the same as that in the acid alone. The reaction velocity in 0.00176 *N* sulfuric acid alone at 20.7°(±0.2°) was found to be 0.05310; the reaction velocities at the same temperature in 0.00176 *N* sulfuric acid containing 0.416 molal magnesium sulfate and in the same acid containing 0.416 molal potassium sulfate were respectively, 0.06006 and 0.09100. The color tint in each instance corresponded with that previously observed in the case of like reaction velocities with varying concentrations of hydrochloric acid.

The abnormal behavior of sulfates in catalyses, in general as compared with that of the salts of the monobasic acids, has been observed by several investigators.[2] An explanation of the phenomenon is undoubtedly to be sought, as suggested by Euler, in the tendency of the neutral sulfate to form the acid sulfate under the conditions of the experiment and thus to effect a slight decrease in the acidity of the solution.

6. Discussion of the "Neutral Salt" Effect.—The behavior of neutral salts in the catalysis of the rosaniline dyes is a remarkable one. It corresponds in general, however, to the effect of such salts as observed by Arrhenius, Euler, Spohr, Stieglitz, Acree and others[3] in such catalyses as the inversion of cane sugar and the saponification of esters. While it seems wise, for the present, to defer full discussion of the results obtained until further quantitative data are secured, a brief consideration of some of the hypotheses advanced to account for the "salt effect" in general may not be out of place.

As was suggested in the investigations of Arrhenius and Euler[4] the salt acceleration in the case of such catalyses as the inversion of cane sugar is probably largely to be ascribed to an increased ionization of water as well as of other electrolytes in the presence of the neutral salt. This is possibly due, as Stieglitz[1] has emphasized, to an increase in the ionizing power of the solvent from the presence of the strong electrolyte.

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[1] *Z. physik. Chem.*, 4, 239 (1889).

[2] Spohr, *Z. physik. Chem.*, 2, 195 (1888). Euler, *Ibid.*, 32, 355 (1900).

[3] See previous references.

[4] Arrhenius, *Z. physik. Chem.*, 31, 197 (1899); *Z. Electrochem.*, 6, 10 (1900). Euler, *Z. physik. Chem.*, 32, 348 (1900).

This explanation is unquestionably a natural one and may possibly serve to account for the "salt effect" in the catalysis studied in this paper. In the determinations in which hydrochloric acid was used (see pages 88-89), the dilution was such that the acid may be regarded as almost completely ionized in the aqueous solution alone. The only electrolytes left for consideration (aside from the salt itself), are, consequently, the water and the dye.

Now, as regards the solvent, it may be noted that any moderate increase in the dissociation of water would not lead to a large increase in the concentration of the H^+ ion. And even though the effect of both H^+ and OH^- ions from such dissociation is in the direction of diminishing the speed of this reaction, it seems difficult to understand how alterations in the reaction velocity, corresponding to such an increase in the concentration of the H^+ ion (200% and more) above that of the acid present, can be caused solely by an increased ionization of water in the presence of electrolytes.

We are, consequently, led to consider the dye. As regards the methyl violet, it may be noted that the condition of equilibrium between carbinol and dye stuff is not a simple one. The three amine groups present the possibility of mono-, di- and tri-acid salts and these must all be taken into consideration in any equilibrium between carbinol and dye in the presence of excess of acid. While this is true, the effect of a heightened ionizing power of the solvent, through the influence of neutral salts, may possibly be safely regarded as producing an alteration in equilibrium between carbinol and quinoid forms equivalent to that resulting from an increase in concentration of H^+ ion.

Of interest in this connection is the effect of a neutral salt upon a neutral solution of a rosaniline dye. As I have already shown, the addition of a chloride such as sodium chloride to a solution of a dye of this series containing a little hydrochloric acid, causes a shift of color tint in the direction effected by an increase in the concentration of the H^+ ion.[2] Addition of such a salt to a *neutral* solution of such a dye does not apparently affect the color tint.

A number of investigators have suggested the possible formation of complex ions on the addition of salts; while Acree has called attention to the possible participation of the non-ionized salt in a catalysis.[3] That an undissociated electrolyte may act as a catalytic agent, I have, indeed, shown[1] in the case of the cinchona alkaloids, where the speed of the conversion is found to be a function of the molecular concentration of the undissociated organic acid. The experimental data are, however, as yet insufficient to enable us to pronounce upon the merits of either of these hypotheses as applied to the action of salts in this catalysis.

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[1] Stieglitz, THIS JOURNAL, 32, 224. "Qualitative Chem Analysis," 1911, page 109.

[2] See also Szyszkowski, *Z. physik. Chem.*, 58, 420 (1907)

[3] *Am. Chem. J.*, 48, 365 (1912).

The hypothesis considered by Goldschmidt, and others,[2] in explaining the "neutral salt effect" regards a possible parallel action of ions and of undissociated molecules. This has been studied by Stieglitz in the case of the imido-esters. Such an hypothesis might be applied to the ionized and non-ionized molecule of the rosaniline dye, but here again the experimental data are insufficient to lead to any conclusion.

A possible factor in the salt effect, to which I believe attention should be called, is the increased mobility of the H^+ ion resulting from the presence of a salt. As shown by Nernst[3] and later developed by Planck[4] and by Pleijel[5] the diffusion constant of hydrochloric acid is found to increase in salt solutions of increasing salt concentration. However this may be accounted for, the resulting dynamic effect of this increase would naturally be a heightening of the activity of the H^+ ion.

7. The Speed of the Reaction as a Dynamic Method in Determining the Concentration of the H^+ Ion.—The action of a neutral salt in shifting the color tint of a dye as noted above, indicates how misleading the results may be in employing a colorimetric method such as that of Salm[6] in estimating under such circumstances the concentration of the H^+ ion in a solution, when no account is taken of the "salt effect." Even in the absence of salts, the static method of Salm leaves much to be desired from the standpoint of accuracy.

While subject to the same disturbing influence of neutral electrolytes, the speed of the conversion of the carbinol base into the quinoid dye naturally suggests itself as a kinetic method for measuring the concentration of the H^+ ion in the absence of appreciable quantities of salts. Although in no way presenting the wide range offered by the inversion of cane sugar or the saponification of an organic ester, nor possibly the accuracy, obtainable through the decomposition of diazo-acetic ester,[7]

[1] Biddle, *Ber.*, 45, 2832 (1912).

[2] Goldschmidt, *Z. physik. Chem.*, 70, 627 (1910); 81, 30 (1912); *Z. Elektrochem.*, 17, 684 (1911). Bredig, *Z. Elektrochem.*, 18, 535 (1912). Snethlage, *Ibid.*, 18, 539 (1912). Acree and his coworkers, *Am. Chem. J.*, 48, 353 (1912); 49, 116, 127, 345, 369, 474 (1913). Stieglitz, THIS JOURNAL, 34, 1689 (1912).

[3] *Z. physik. Chem.*, 2, 613 (1888).

[4] Planck, *Wied. Ann.*, 40, 56 (1890).

[5] Pleijel, *J. physik. Chem.*, 72, 1 (1910).

[6] *Z. physik. Chem.*, 57, 471 (1906).

[7] Bredig, *Verhandlungen des Naturhistorisch—Medizinischen Vereins zu Heidelberg, N. F.*, 9, 1 (1907).

yet the ease with which measurements may be made invites a brief consideration of the possibilities presented.

A study of the graph in Fig. 2, as we have already noticed, reveals the fact that with H^+ ion concentrations greater than 5.5×10^{-3} molal, the variations in speed of the reaction with varying concentration of the H^+ ion are too slight to render them of any value in determining such concentrations with any degree of accuracy. On the other hand, variations of H^+ ion concentration within the range of 1.55×10^{-3} to 3.4×10^{-4} are accompanied by such marked increase in the speed of color change that, within this range, the latter might be employed to detect very slight variations in the former. Within this range, however, the speed experiences marked alteration with slight variations in temperature. Measurements for comparison, consequently, must be made at some fixed temperature, otherwise large error will be introduced.[1] The temperature effect becomes less in passing from 1.55×10^{-3} to 5.5×10^{-3} molal concentration of the H^+ ion, and within this range such concentration should be determined from the speed of the reaction with a fair degree of accuracy.

Within a limited range of concentration of H^+ ion, the speed of this color change may thus be used to determine the value of the concentration. Within this range, the degree of accuracy much exceeds any possibility presented by any static colorimetric scheme such as that worked out by Salm. Unfortunately, however, the range in the case of any one indicator is small. At the same time the possibility presents itself of extending this range through a careful study of a number of basic dyes such as rosaniline, pararosaniline, and malachite green on the one hand and of acid dyes such as phenolphthalein and thymolphthalein on the other. Work is being carried forward in this direction in this laboratory.

To determine something regarding the possible accuracy of this method in estimating the concentration of the H^+ ion, measurements were made of the speeds of reaction in a number of acid solutions and the calculated concentration of the H^+ ion was compared with that derived from the graphs of Figs. 1 and 2 The quantity of salt present in each case was too small to diminish, to any noticeable extent, the speed of the reaction through the "neutral salt effect." The degree of dissociation, a, of one gram-molecule of the weak acid in volume, V, in the presence of its salt was calculated from the equation, $a(a + nb)/(1 - a)V = K$, where n equals the number of gram-molecules of the salt with the degree of dissociation, b, in volume, V.[2] The potassium acetate formed by the

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[1] In the experimental determinations made in this paper temperature variations, amounting to ±0.2° are allowed for, although in many cases the variation was less than this.

[2] Arrhenius, "Theories of Solutions," page 166.

TABLE XIX.

Acid.	Salt.	Reaction velocity at 19.5°(±0.2°)C.	Concentration of H+ ion from observed reaction velocity.	Calculated concentration of H+ ion.
1. Hydrochloric acid (0.00176 molal)........	Potassium chloride (0.00242 molal)	0.05010	0.00160 molal	0.00176 molal
2. Acetic acid (0.8333 molal)........	Potassium acetate (0.00268 molal)	0.02124	0.00272 molal	0.00282 molal
3. Acetic acid (0.4166 molal)...	Potassium acetate (0.00268 molal)	0 05401	0.00150 molal	0.00175 molal
4. Acetic acid (0.2083 molal)...	Potassium acetate (0.00268 molal)	0 07843	0.00105 molal	0.00125 molal
5. Acetic acid (0.8333 molal)	Potassium acetate (0.00268 molal) Sodium acetate (0.00833 molal)	0 06540	0 00138 molal	0 00136 molal

alkali from the methyl violet in examples 2–5, is assumed in each case to be completely dissociated, while the minute quantity of acetic acid neutralized by the alkali in these cases is ignored (the error introduced by these assumptions is negligible). The sodium acetate added in example (5) is regarded as dissociated to the extent of 90%. Following are the results obtained:

Up to the present time the dyes of the triphenylmethane series which have been studied in this catalysis are those possessing two and three NH_2 groups. To determine the possible influence of the several NH_2 groups upon this reaction velocity the study is being extended to monaminotriphenylcarbinol and its derivatives.[1] In these simpler cases the complex conditions introduced by the formation of diacid (and triacid) salts will naturally be eliminated. The results obtained here will, we trust, throw further light upon the catalysis of the cinchona alkaloids, in which substances the elimination of the "quinoline nitrogen" or second nitrogen atom was not feasible without destroying the nature of the alkaloid complex.

Study is, furthermore, in progress in conjunction with Messrs. Ludwig, Rosenstein and L. Q. Adams, of this laboratory, with regard to the absorption spectra of solutions of a rosaniline dye containing increasing quantities of an acid, in the hope of securing fuller information as to the existence and nature, in the solution, of the mono-, di- and tri-acid salts of the dye.

Summary.

1. In the conversion of a rosaniline dye from the colorless to the colored form, the speed of the reaction in the approach to the equilibrium color is a function of the diminishing concentration of the H^+ ion.

2. The speed of the reaction, unlike that of the conversion of the cinchona alkaloids into their toxins, is independent of the nature of the acid present and is consequently not, as in the latter case, a function of the molecular concentration of the acid.

3. The speed of the reaction increases with rise of temperature, the rate of increase rising with diminishing concentration of the H^+ ion.

4. Neutral salts in diminishing or increasing the degree of dissociation of a weak acid correspondingly increase or diminish the speed of the reaction in the presence of such an acid.

5. The "neutral salt" effect gives rise to a shift in color and a diminution in the speed of the reaction corresponding exactly with the results produced by an increasing concentration of the H^+ ion.

6. Within certain limited ranges the speed of the reaction may be used

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[1] Work in this direction is being carried on by Mr. L. W. Stebbings of this laboratory.

as a dynamic method for determining, with fair precision, the concentration of the H^+ ion.

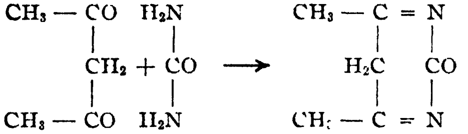
BERKELEY, CALIF.

THE CONSTITUTION OF ACETYLACETONE-UREA.

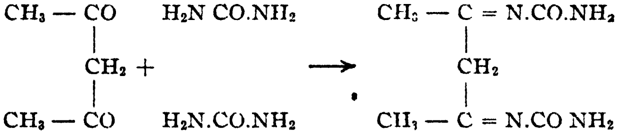
BY WILLIAM J. HALE.

Received October 16, 1913.

As first reported by Evans[1] and shortly afterwards by A. and C. Combes,[2] the condensation of acetylacetone and urea may proceed in either of two ways. The more stable product, called by Evans, acetylacetone-urea and the second, called diurimidoacetylacetone, were described at length in a second contribution.[3] The condensations were looked upon as proceeding in the following manner:



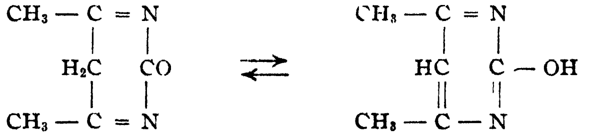
[1]



[4]

The ease with which this acetylacetone-urea gave salts with heavy metals was thought to be due to its ready transformation into an enolic form [2]:

[1]



[2]

If this assumption were correct we should have, for consideration, a 2-hydroxypyrimidine; a compound of the type described by Hale and Brill[4] in work upon urea and a β-dialdehyde. With the exception of certain uracil derivatives,[5] which may exist in such tautomeric form, we note a marked absence of description of 2-hydroxypyrimidines in the literature. It seemed well, therefore, to undertake further investigation upon this product of Evans' in order to study the distinctive properties of 2-hydroxypyrimidines as a class.

According to Evans, the usual reactions characteristic of an hydroxyl group failed entirely in this compound; neither benzoyl nor acetyl esters could be prepared; no definite compound could be obtained by the action of methyl iodide upon the dry silver salt; and the alkali salts were obtainable only with difficulty by reason of marked hydrolysis. From such evidence we are led at once to the conclusion that a true imino base is most likely present.

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[1] *J. prakt. Chem.*, [2] 46, 352 (1892).

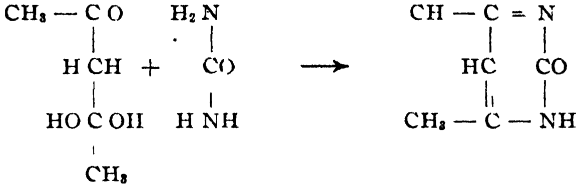
[2] *Bull. soc. chim.*, [3] 7, 791 (1892).

[3] *J. prakt. Chem.*, [2] 48, 489 (1893).

[4] THIS JOURNAL, 34, 82 (1912).

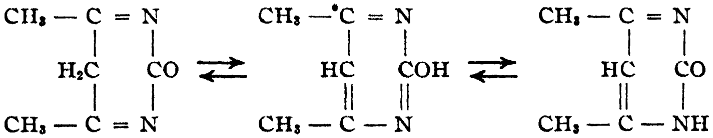
[5] *J. prakt. Chem.*, [2] 47, 201 (1893).

A very careful study of the condensation products of acetylacetone and urea has been conducted by de Haan.[1] His work indicated the imino formula [3] as a possible structure for acetylacetone-urea, and a mode of condensation represented as follows:



[3]

Tautomeric, with this product, de Haan assumed that a quinoid form [1] must be considered in order to account for certain color changes in the compound itself and in its derivatives. He does not, however, argue to the exclusion of the enolic form proposed by Evans, hence we have, for our consideration, the following possible tautomeric formulas:



(1) (2) (3)

As first prepared, acetylacetone-urea crystallizes from water with 2 molecules of water of hydration. These crystals, prepared with care and without access of light, are perfectly colorless. When, however, this aqueous solution falls under the influence of heat, or light, lemon-yellow crystals are obtained; the same product as that which results upon exposing the colorless crystals to direct sunlight. Both forms of crystals lose their two molecules of water by long standing in the air but better over calcium chloride. de Haan has shown conclusively that a colorless nitrate can be prepared from the colorless form of crystals, and likewise a red-colored nitrate from the colored form. From a series of optical measurements upon the colorless and colored forms of acetylacetone-urea scarcely no difference could be detected between the two. The relation between the colorless and colored forms may well be represented as in [3] and [1], respectively. Though de Haan gives preference to the imino form, he maintains that the second possible structure for the colorless compound, namely an enolic form of dimethylketopyrimidine [2], must be considered. This latter is, of course, the structure already proposed by Evans to explain the tendency toward salt formation in the compound. Without doubt, we may conclude that the original formula assigned by Evans to acetylacetone-urea, the quinoid form [1], may be taken to represent the colored product. For the colorless substance there remain therefore the two possibilities [2] or [3], for which we shall select that one best substantiated by the facts at hand.

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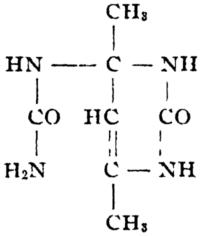
[1] *Rec. trav. chim.*, 27, 162 (1908).

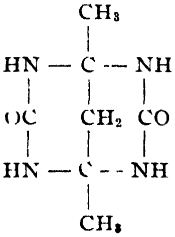
Evans prepared acetylacetone-urea by allowing urea and acetylacetone to react in alcoholic solution in the presence of a large quantity of either concentrated sulfuric or hydrochloric acid. From the corresponding salts, which crystallize out, the free substance was easily obtained in aqueous solution by the action of barium carbonate or silver oxide, respectively. In place of this acetylacetone-urea Evans found that, by use of a much smaller quantity of acid and a relatively large portion of urea (2 molecules), an entirely different product resulted, a so-called diurimido-acetylacetone in the form of the corresponding acid salt. To this product Evans assigned the structure [4]. In solubilities and melting point (197°) it was found not much unlike those of acetylacetone-urea. When the hydrochloride in aqueous solution was warmed with silver oxide, acetylacetone-urea and free urea were obtained. Though the presence of one free ureide group may thus be confirmed, the presence of only one is not established. There remained, therefore, the supposition that we had here two free ureide groups until the work of de Haan gave us the correct interpretation of the structure of this compound, namely, that of a monoureide of a ring substance, this same acetylacetone-urea ring.

de Haan best prepared this product by allowing an absolute alcoholic solution of urea (2 molecules) and acetyl acetone (1 mol) to stand for several days. The colorless crystals separating out are practically insoluble in alcohol, but fairly soluble in water. This substance is the principal product obtained when acetylacetone and urea are allowed to react without any large quantity of acid condensing agent. The constitution [5] assigned by de Haan makes it a 6-ureido-4,6-dimethyl-2-keto-2,3,6,1-tetrahydropyrimidine, or as de Haan reported, a 4,6-dimethyl-2-ketopyrimidine-urea.

Readily acted upon by nitric acid with evolution of gas, the presence of only one free urea group is indicated; the residue is the nitrate of dimethylketopyrimidine. Again, by the action of strong alkali, the liberation of ammonia corresponded with the decomposition of one free urea group, and gave a residue of dimethylketopyrimidine alkali salt As might be expected, a small quantity of crystals of this dimethylketopyrimidine-urea were obtained when unimolecular quantities of dimethylketopyrimidine and urea reacted together.

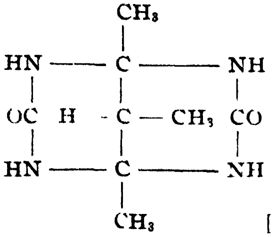
According to the method of M. Combes, complete solution between acetylacetone and urea is effected when they are warmed together for several hours upon a water bath. Upon cooling and digestion of the crystalline mass with alcohol, a small quantity of an insoluble product, melting at 290°, is left undissolved. From the alcoholic solution, however, a considerable amount of the dimethylketopyrimidine-urea is obtained by crystallization. The insoluble substance is obtained in somewhat better yield when acetylacetone and an excess of two molecules of urea are allowed to stand in aqueous solution at room temperature. The yellow tinged crystals separating out were investigated by de Haan and called 2,4-diureinopentane [6].

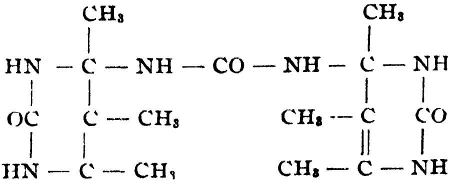

[5]


[6]

After somewhat longer standing of this aqueous reaction-mixture, a small quantity of crystals of dimethylketopyrimidine-urea make their appearance. This diureinopentane is produced in small quantities only. It is not acted upon by cold nitric acid, and thus the absence of a ureide chain is confirmed. By prolonged action of nitric acid or boiling with dilute acid, decomposition of the molecule ensues and dimethylketopyrimidine nitrate results. This production of diureinopentane from aqueous reaction-mixtures recalls somewhat the condensation between urea and diacetyl leading to the production of dimethylglycoluril,[1] the properties of which differ in no marked extent from this substance.

de Haan further studied the condensation of urea with the two methyl derivatives of acetylacetone. Monomethylacetylacetone condensed very slowly with urea in the presence of sulfuric acid, but better by simple fusion of the two substances alone. In aqueous solution they also condensed and yielded both 2,4-diureino-3-methylpentane [7] and 4,5,6-trimethyl-2-ketopyrimidine-urea [8], the latter the more soluble in alcohol:


[7]


[8]

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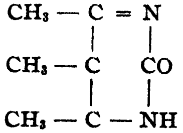
[1] Franchimont and Klobbie, *Rec. trav. chim.*, **7**, 251 (1888). See also Widman, *Ber.*, **19**, 2477 (1886).

Either of these products, practically colorless, when carefully treated with nitric acid, gives the yellow crystals of 4,5,6-trimethyl-2-ketopyrimidine [9] as nitrate.



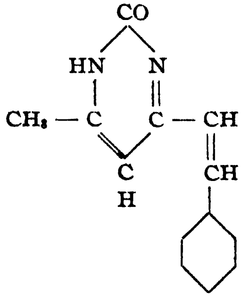
[9]

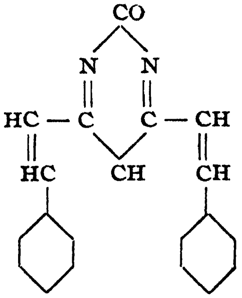
The free product (melting point 209–10°) is colorless and resembles the dimethyl derivative previously described. The tendency here to develop color is only slight; neither by heat upon its aqueous solution nor by action of methyl iodide upon its alkali salt is any color change observed. Nitric acid alone seems able to bring about this change to a yellow salt.

In the study of dimethylacetylacetone and urea, colorless crystals of 2,4-diureino-3,3-dimethylpentane were obtained in small quantity. By the action of nitric acid the methyl groups are lost and possibly a 4,6-dimethyl-5,5-dihydroxy-2-ketopyrimidine produced.

Extensive work upon the condensation of aldehyde with this acetylacetone-urea was carried out by Stark.[1] It was thought that the methylene group of the quinoid form [1] would readily lend itself to condensation with aldehydes. Stark, however, found that the methyl groups, since they were attached to carbon atoms possible of double ties with another atom, entered more readily into this condensation; a tendency, according to the structure, that may be compared with α-quinaldine reactions. With piperidine as condensing agent, one which favors strongly the ketopyrimidine formula, the monobenzal, obtained from benzaldehyde and the pyrimidine, appears in colorless form, showing therefore that the condensation must have proceeded from formula [3] to the structures shown in [10]. It is readily soluble in alcohol, and, under the influence of light, heat and possibly benzaldehyde itself, it goes over into the quinoid form, whereupon a second methyl group becomes possible of reaction, giving thus a golden yellow dibenzal of formula [11]:

[10]





[11]

With *p*-oxybenzaldehyde and vanillin, the first condensation products are only difficultly soluble and hence do not readily tautomerize. Consequently the monobenzal derivatives only are formed. These mono derivatives, however, develop color with acids, and thus enter into quinoid form.

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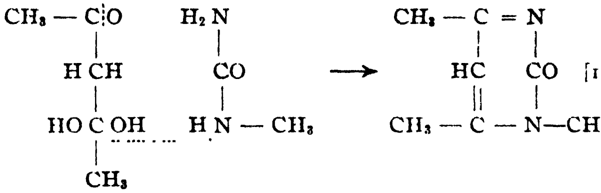
[1] *Ber.*, **42**, 699 (1909).

Further confirmation of the quinoid structure for acetylacetone-urea, in colored form, has been clearly presented by Stark in his later contributions.[1] The work of Majima[2] upon alkylguanidines and acetoacetic ester would indicate also this quinoid structure for the colored product. So also this structure has been indicated by St. Angerstein[3] and again by Wheeler and Jamieson[4] from entirely different sources.

Throughout the work of Evans, de Haan, Stark, and others no mention is made of investigating an alkyl derivative of urea in connection with the ketone. It seemed advisable, therefore, to bring into this study the possible reactions between acetylacetone and monomethylurea If Evans' theory of a diurimido product were correct then we might hope to obtain the corresponding symmetrical dimethyl-diurimido-acetylacetone (cf. 4). Again, by condensation in alcoholic solution with great concentration of acid, we should obtain an acetylacetone-methylurea [12] in the following manner:



[12]

Though the greatest care was exercised in order that the condensation between these substances might proceed in the presence of only the smallest amount of acid (method of Evans' above), scarcely enough to form the corresponding salt, there separated from the alcoholic solutions in each and every case the same colorless crystalline mass as was obtained when greater concentrations of acid were employed. Analyses and properties indicated that the product was not a simple ureide but one of ring structure, and this again not of the possible quinoid form of acetylacetone-urea, but a methyl derivative of the imino form [3]. If we retain the name acetylacetone-urea for the colored or quinoid structure we may logically call the imino form a dimethyl-2-ketopyrimidine and consequently this new product will be a 3,4,6-trimethyl-2-keto-2,3-dihydropyrimidine [12].

In fact the ease, with which this pyrimidine derivative is formed, would suggest that even with urea a similar condensation to ring structure should

[1] *Ber.*, 42, 708 (1909); *Ibid.*, 42, 1126 (1909); *Ann.*, 381, 143 (1911).

[2] *Ber.*, 41, 176 (1908).

[3] *Ibid.*, 34, 3756 (1901).

[4] *Am. Chem. J.*, 32, 356 (1904).

not be unexpected in the presence of mild condensing agents; a result exactly in keeping with de Haan's conclusions that Evans' diurimidoacetylacetone is merely a derivative of acetylacetone-urea, which latter is really the first product of the reaction.

When methylurea and acetylacetone are warmed together on the water bath or allowed to stand either in alcoholic or aqueous solutions, no marked reaction takes place, though from alcoholic solutions a small quantity of the methylpyrimidine could be removed. With this condensation proceeding so well in the presence of acid, it appears most difficult to accomplish without the acid condensing agent, a result not unlikely with alkyl ureas. In similar manner many efforts were made to condense unsymmetrical dimethylurea with acetylacetone by means of acid, and thus possibly obtain a simple ureide of chain structure, but in each case no positive results were obtained. Though such condensation may possibly be effected by other means, the failure in presence of acid is the point of comparison here made. If a mono-ureide of the ketone is produced, its stability seemingly is not assured till further condensation into ring form is effected.

The product of the condensation between methylurea and acetylacetone is much more soluble in the ordinary solvents than the corresponding ketopyrimidine of Evans. Reactions indicate the absence of any free ureide group. The position of the methyl group upon the 3-N atom was confirmed by the Herzig-Meyer reaction by which methyl iodide was given off only at very high temperatures. This trimethylketopyrimidine, unlike the dimethyl derivative, refuses altogether to give metallic salts; there can be then no ionizable hydrogen. With the N-alkyl firmly fixed the reactions for a tertiary nitrogen atom always persisted under many possible reactions.

The ease of formation of this trimethylketopyrimidine, without the production of an intermediate diurimido product, argued strongly for a similar procedure when urea and acetylacetone entered into condensation, though here with less speed than in the former case where an imino hydrogen is well situated to effect the ring closing. There is also no tendency for the methylurea condensation product to combine with another molecule of the alkyl urea to produce a possible pyrimidine-methylurea in analogy with the urea condensation [cf. 5]. The loss of acid characteristics in the trimethylketopyrimidine possibly explains this further inactivity toward a second molecule of the base, urea, in effecting this result.

With the structure of the trimethylketopyrimidine so well in hand, it appeared all the more possible to establish the structure of the dimethylketopyrimidine of Evans by a simple methylation. If the methyl group entered upon an hydroxyl, as shown in the constitution [2] supported both by Evans and de Haan, we should have a trimethyl derivative entirely different from the one just described. If, on the other hand, the methylation took place on the imino group, as shown in [3], we should have accordingly a 3,4,6-trimethylketopyrimidine of the identical structure as that product obtained from methylurea and acetylacetone, constituting a clear and direct proof of the structure of the colorless dimethylketopyrimidine.

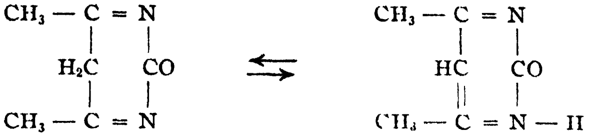
Attempts to carry out this methylation of Evans' product were at first unsuccessful. Both Evans and de Haan describe the failure attending the reaction of alkyl iodides upon the silver or alkali salts of the ketopyrimidine. In such cases, however, a deep red colored product could be separated from the reaction-mixture. Attempts were then made to methylate, by means of dimethylsulfate, but the product here, as in the previous method, turned quickly to a deep red color. The residue from the action of methyl iodide upon the silver salt was indeed beautifully crystalline but gave, in aqueous solution, a copious yellow precipitate of silver iodide when treated with a soluble silver salt. This presence of iodide-ion indicated an ammonium salt and possibly here an alkyl iodide addition product to one of the nitrogen atoms. Further work showed the correctness of this view. In order to test further this possibility, a methyl alcoholic solution of the free dimethylketopyrimidine was warmed over a water bath with methyl iodide. After a short time the solution, upon spontaneous evaporation, gave colorless needle-like clusters of crystals. These, when removed and analyzed, confirmed our supposition and established the substance as a simple addition product of the free dimethylpyrimidine and methyl iodide. In the action of this halide upon the silver salt of the pyrimidine, there is no doubt a first formation of trimethylketopyrimidine and then, later, an alkyl iodide addition product of the latter.

By reason of this great tendency to form addition products with alkyl halides and acid salts, an entirely different method for methylation was undertaken. This method consisted in the use of diazomethane of v. Pechmann. The anhydrous dimethylketopyrimidine was dissolved in chloroform (or methyl alcohol) and the vapors of diazomethane led into the solution, after which the vessel was closed and set aside for an hour or more. Upon spontaneous evaporation of this solution, there appeared colorless crystals of trimethylketopyrimidine melting at 63°, identical in all respects with that trimethyl derivative obtained by condensation of methyl urea and acetylacetone It is thus seen that the alkylation by diazomethane takes place upon the imino hydrogen atom. It matters not if the starting point be the dried yellow quinoid form, the acetylacetone-urea according to Evans' formula, as the tautomeric imino form is readily produced and methylation proceeds in the manner outlined. If the supposition of Evans and de Haan were correct and a possible hydroxyl group here present, then this action of diazomethane would lead at once to a methoxyl derivative. The product, however, does not contain a methoxyl group and, hence, we conclude that the colorless form of the dimethylketopyrimidine exists alone in the imino type.

The trimethylketopyrimidine obtained by alkylation showed a somewhat greater tendency to take on a red color than that product from the condensation of methyl urea and acetylacetone. Though the cause of the red color is unknown it has been thought due to a possible tautomerization, or shifting, of the methyl group to the 5-carbon atom. The product thus formed would coincide exactly in constitution with the trimethyl derivative [9] of de Haan, but as this latter has been shown to be even less colored than the free dimethylketopyrimidine, the hypothesis lacks substantiation. The trimethylketopyrimidine remains much longer colorless when confined *in vacuo*.

In order, now, to prove the constitution of the addition product resulting from the action of methyl iodide upon dimethylketopyrimidine there remained only to treat this addition product with alkali and liberate, if possible, a trimethyl derivative. The chloroform extract of this methyl iodide addition product, when treated in aqueous solution with potassium hydroxide, gave upon spontaneous evaporation, the reddish tinged crystals of the 3,4,6-trimethyl-2-ketopyrimidine, thus proving that the addition product can readily be converted into the trimethyl derivative, and further indicating the possible addition of methyl iodide to that nitrogen in the imino group.

The absence of an hydroxyl group in Evans' product is no longer in question. The complete failure of acetylacetone-urea to react with acetyl chloride or benzoyl chloride led to this early assumption. The presence, however, of an imino group in our accepted formula, naturally leads to the supposition that benzene sulfochloride (Hinsberg's test) should react with this substance. Practically the only exceptions to Hinsberg's reaction are just those of this type of compounds where a secondary nitrogen atom is situated adjacent to a carbonyl group and functions thus both as acid and base. Repeated and persistent efforts in carrying out this test, both for the colored and colorless forms of the dimethylketopyrimidine, failed to give any appreciable quantity of product insoluble in the alkali. This failure of reaction, however, can not be construed, as just pointed out, to negative other results. The tautomerism between the colored acetylacetone-urea and its colorless form, 4,6-dimethyl-2-ketopyrimidine, must lie between the formulas here shown:



Acetylacetone-urea.
(The accepted name for 4,6-dimethyl-2-keto-2,5 dihydropyrimidine.)

4,6-Dimethyl-2-keto-2,3-dihydropyrimidine.

Experimental Part.

Acetylacetone-urea (*1*).—The method of preparation was, in general, that described by Stark.[1] Ten grams of urea were dissolved in 160 grams of alcohol and to the cooled solution 10 grams of acetylacetone and 30 grams of concentrated sulfuric acid added as quickly as possible. The well-mixed solution (set aside in ice-box) deposited crystals within a few hours; all told, about 12 grams of the sulfate salt were obtained. When a solution of this sulfate is boiled for a few minutes with barium carbonate and the clear filtrate evaporated nearly to dryness over a water bath, there separate, upon standing, large yellow prisms of the acetylacetone-urea [1], containing two molecules of water of crystallization.

4,6-Dimethyl-2-keto-2,3-dihydropyrimidine (*3*).—When the reaction-mixture just described for the preparation of acetylacetone-urea is set aside in the dark and the salt separating out dissolved in a small quantity of water and digested with an emulsion of freshly precipitated barium carbonate, a clear filtrate, free from sulfate-ion, is easily obtained. This solution, by spontaneous evaporation in the absence of light, gives beautiful colorless crystals of the dimethylketopyrimidine.

0.4782 gram air-dried salt lost over $CaCl_2$ 0.1082 gram H_2O.

Calculated for $C_6H_8ON_2.2H_2O$: H_2O, 22.50%. Found. H_2O, 22.62%.

The colorless product, just as the colored product, contains exactly two molecules of water of crystallization. The two products, as already stated, differ scarcely at all in crystalline form. de Haan describes them as monoclinic, but in the case of the colorless, there is a slightly greater difference in the angles between the faces in the zone of the orthodiagonal than in the other. They each melt at 197°.

A potassium salt can be prepared from an aqueous solution of these products. It is, however, completely decomposed by the action of carbon dioxide in the air. The application of Hinsberg's test by warming a small quantity of these products with benzene sulfochloride and sufficient alkali, gave no appreciable quantity of oily or insoluble matter. The white insoluble silver salt is readily prepared by adding silver nitrate to an aqueous solution of either the yellow or colorless products. The red crystalline substance, obtained by action of methyl iodide upon the silver salt, suspended in methyl alcohol, is very soluble in water. It showed reactions for an iodide and is undoubtedly a methyl addition product of the trimethylketopyrimidine first formed. Mercuric chloride also gives an insoluble salt with the pyrimidine. Platinic chloride does not give an addition product.

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[1] *Ber.*, 42, 699 (1909).

Acetylacetone-urea Methyl Iodide Addition Product.—$C_6H_8ON_2.CH_3I$.—One gram of the well dried yellow acetylacetone-urea was dissolved in 10 to 25 cc. of methyl alcohol and a few grams of methyl iodide added. The contents of the flask were heated to boiling for an hour or two under a reflux condenser, and afterwards allowed to evaporate in vacuum desiccator. The colorless crystals of the addition product slowly separate, but upon standing in the air, readily develop a red color. The yield was 1.9 grams, or 88% of the theoretical value.

Calculated for $C_7H_{11}ON_2I$: I, 47.71; found: 47.83.

Methylation of Acetylacetone-urea.—As previously stated, the action of methyl iodide upon the silver salt of the dimethylketopyrimidine, as well as the action of dimethyl sulfate upon this substance, gave no satisfactory results, owing to the formation of addition products and deep coloration which these underwent. The use of diazomethane, however, proved most satisfactory. In accordance with the method of v. Pechmann[1] the yellow vapors of diazomethane were led into a cooled chloroform solution of the dried acetylacetone-urea and the vessel stoppered and allowed to stand for an hour or two. Upon spontaneous evaporation of the solution in a vacuum desiccator, colorless crystals of the free trimethylketopyrimidine were obtained. Recrystallized from benzene, the product melted at 63° and proved identical in all other respects with the trimethylketopyrimidine prepared from methylurea and acetylacetone as described below. When the two were mixed the melting point of the mixture remained constant at 63°.

Condensation of Methylurea with Acetylacetone.—Six grams of methyl urea and 9 grams of acetylacetone were dissolved in 30 cc. of alcohol and cooled. To this mixture, 30 grams of concentrated sulfuric acid were added and the flask with its contents set aside in a cool place. The further addition of a little alcohol, in the course of a day or two, increases somewhat the total precipitation of crystals. At the end of three days 16.6 grams of crystalline product had separated. This product, a sulfate, was dissolved in a small quantity of water and the solution neutralized with sodium hydroxide, and then extracted with chloroform. From the chloroform extract 9.4 grams of the colorless base were obtained, *i. e.*, practically 84% of the theoretical amount of trimethylketopyrimidine possible from the weight of methylurea taken. In the form of sulfate, this product crystallizes well from alcohol.

H_2SO_4 calculated for $C_7H_{10}ON_2.H_2SO_4$: 41.53; found: 41.89.

[1] *Ber.*, **28**, 851 (1895).

The condensation of methylurea and acetylacetone was also conducted in the presence of only sufficient sulfuric acid to form the calculated amount of sulfate, and at the same time an excess of the urea (2 mol) used. It was hoped that, by this means, a compound of the type described by Evans as a diurimido derivative might be prepared. In all cases the crystalline product obtained was no greater in weight than that where molecule to molecule was used. By analysis, the salt, crystallized from alcohol, accorded with the previous results:

H_2SO_4 calculated for $C_7H_{10}ON_2.H_2SO_4$: 41 53; found: 41.98.

We may conclude, therefore, that the pyrimidine ring is formed at once in this acid reaction-mixture. The free substances obtained by neutralizing the sulfate salt, obtained either by the use of concentrated acid or by this latter method, melted at the same point, 63°, and proved identical. 3,4,6-Trimethyl-2-keto-2,3-dihydropyrimidine is readily soluble in water, alcohol, chloroform, acetone or acetic ester; fairly soluble in ether, benzene, carbon disulfide; and insoluble in ligroin. It crystallizes well from benzene and melts at 63°.

0.2055 gram substance gave 0.4593 gram CO_2 and 0.1387 gram H_2O.
0.1634 gram substance gave 30.9 cc. N_2 (25°, 739.3 mm. over H_2O).

Calculated for $C_7H_{10}ON_2$:	C, 60.82; H, 7.30; N, 20.31.
Found:	C, 60 95; H, 7.55; N, 20 53.

This product of condensation, as before stated, is identical with the trimethylketopyrimidine obtained by methylation of acetylacetone-urea. It is, however, in a much purer form, requiring but one or two crystallizations for final purification.

The preparation of this trimethylketopyrimidine, by condensation in the presence of hydrochloric acid, was found equally as practical as with sulfuric acid, but with a somewhat longer period of time necessary. The hydrochloride salt crystallizes well from alcohol in colorless prisms.

Calculated for $C_7H_{10}ON_2.HCl$: HCl, 20.88; found: 20.78.

Zeisel's method, for the determination of methoxyl groups, gave negative results with this trimethylketopyrimidine, but at high temperatures, 200–300°, Herzig and Meyer's method succeeded in driving off methyl iodide sufficient to indicate that, at least, one methyl group attached to a nitrogen atom was present in the molecule.

ANN ARBOR, MICHIGAN.

THE RELATION BETWEEN THE BOILING POINT AND COMPOSITION OF A MIXTURE OF ETHYLIODIDE AND ETHYL ALCOHOL.

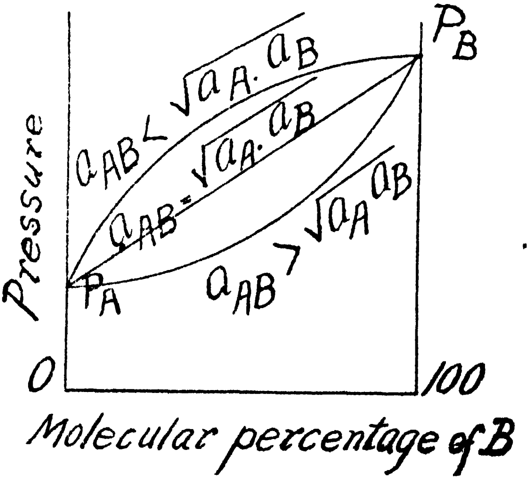
BY SARAT CHANDRA JANA AND JITENDRA NATH SEN GUPTA.

Received October 26, 1913.

The boiling points, or the vapor pressures, of mixtures of liquids have been determined by many investigators. For non-miscible liquids, such as chlorobenzene and water, this can be accurately calculated by the law of partial pressures. The whole pressure at any given temperature is equal to the sum of the partial pressures of the two components at the given temperature. Thus, one can easily calculate the boiling point of the mixture if he knows the composition of the liquid phase and the pressure under which the distillation is carried on. The relative masses of the vapors in a given volume can also be calculated by means of the formula $D_A \times P_A/D_B \times P_B$, where D_A and D_B are the vapor densities and, P_A and P_B are the vapor pressures at any given temperature.[1] The process of steam distillation in the case of high boiling liquids such as glycerol depends on this principle.

In the case of substances which mix together in any proportion, the above rule cannot, however, be applied. In the case of chemically related substances the vapor pressure can be calculated by means of the formula $100\ P = MP_A\ (100 — M)P_B$, where M is the molecular percentage of A, and P, P_A and P_B are the vapor pressures of the mixture and of A and B, respectively at the given temperature. Van der Waals, however, limits the application of this formula to those substances whose critical pressures are equal.[2] Young has calculated the vapor pressure of a mixture of chlorobenzene and bromobenzene by this formula with fairly accurate results.[3]

The boiling point and the molecular composition of such mixtures of liquids can be calculated easily. In order to do this, the vapor pressures of each substance must be known at all temperatures between their respective boiling points under a given pressure p. The percentage molecular composition which would exert a vapor pressure p is then calculated at a series of temperatures between these limits by means of the formula $M = 100\ P_B — P/P_B — P_A$. Finally the values of M must be plotted against the temperatures and the curve thus obtained will give the relation between the boiling point and molecular composition under the pressure p.



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[1] Naumann, *Ber.*, 10, 1421, 1819, 2015, 2099; Brown, *Trans*, 547 (1873)

[2] *Proc. Roy. Acad. Amsterdam*, 3, 170 (1900).

[3] *J. Chem. Soc.*, 81, 768 (1902).

In the case of mixtures of substances which are not closely related to one another the preceding formula cannot be applied. As a general rule it may be stated that the relation between the vapor pressure and the composition of such mixtures is represented by a curve. This relation has been expressed graphically by Galitzine and D. Berthelot as shown above, where $a_{A.B}$ denotes attraction of the unlike molecules and a_A and a_B between like molecules. The deviation of the boiling point of mixtures from straightness has been observed in the case of many substances. As instances of mixtures of maximum boiling points, the following pairs of liquids may be cited—propyl and isobutyl alcohol with water,[1] formic, acetic and propionic acids with pyridine (Zawidoski), hydrochloric acid and methyl ether (Friedel) formic, nitric, hydrochloric, hydrobromic and hydriodic acids with water (Roscoe) also chloroform and acetone (Ryland).

As instances of mixtures of minimum boiling points, we may mention carbon bisulfide and acetone, carbon bisulfide and methyl acetate, acetone and methyl acetate, acetone and ethyl iodide (Ryland).

In a mixture of ethyl alcohol and ethyl iodide the boiling point is found to be much lower than that of either of the two. The boiling point of ethyl alcohol is 77.8°, but a mixture of 87% of ethyl iodide and 13% of ethyl alcohol boils at 61.2° under ordinary atmospheric pressure. The boiling point of ethyl alcohol is gradually lowered by the addition of small quantities of ethyl iodide until a minimum is reached, then it rises again. Similarly, the boiling point of ethyl iodide is lowered by the addition of small quantities of ethyl alcohol. The following table gives the relation between the percentage of ethyl iodide in the mixture and the boiling point.

Percentage of ethyl iodide.	Boiling point	Percentage of ethyl iodide	Boiling point.
26.69	70.2°	97.63	64.0°
35.69	68.8	94.50	62.0
41.38	67.0	90.5	61.5
52.86	64.8	88.35	61.3
57.28	64.0	84.87	61.4
62.70	63.3	78.36	61.9
		69.42	62.2

A curve drawn from the above data gives the relation between the boiling point of the mixture and the percentage of ethyl iodide. A mixture of 87% of ethyl iodide and 13% of ethyl alcohol boils at 61.2° and the mixture will distil off as a homogeneous liquid.

It has been suggested that such mixtures, of maximum and minimum boiling-point curves, are obtained in the case of associating liquids. Ethyl alcohol is a liquid of great molecular association as can be seen from

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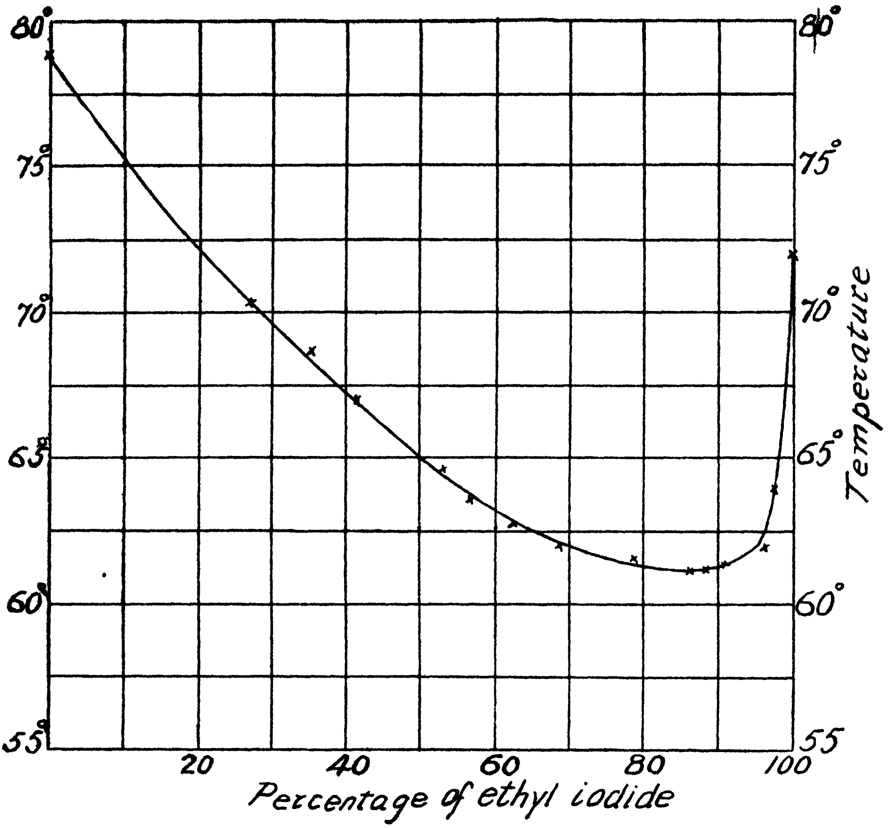
[1] Konowalow, *Wied. Ann.*, 1434 (1881).



capillary measurements, the relation between boiling point and specific cohesion, and also from Traube's volume relations; but ethyl iodide is not an associating liquid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. XII. DERIVATIVES OF ISOCAMPHORIC ACID; DECOMPOSITION PRODUCTS OF ISOAMINODIHYDROCAMPHOLYTIC ACID.[1]

BY WILLIAM A. NOYES AND LLOYD F NICKELL

Received November 26, 1913.

Of the four isomeric amino acids derived from *d*-camphoric acid and *l*-isocamphoric acid, the decomposition with nitrous acid of but one, aminodihydrocampholytic acid, has been thoroughly studied. Noyes and Potter[1] decomposed this acid with nitrous acid and obtained the following products:

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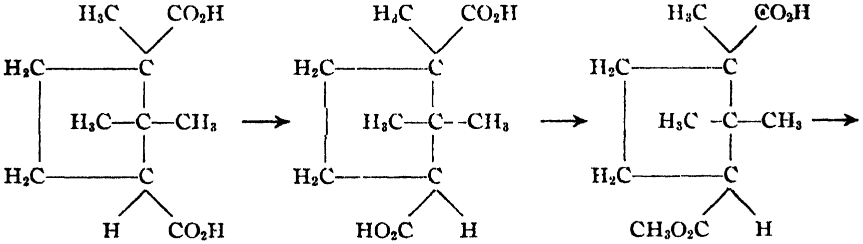
[1] Abstract of a thesis presented by Lloyd F. Nickell in partial fulfilment of the requirement for the degree of Doctor of Philosophy at the University of Illinois.

	Per cent.
Isolaurolene	0.7
d-Campholytolactone	5.3
l-Campholytic acid	12.0
d-*Trans*-hydroxydihydrocampholytic acid	45.0

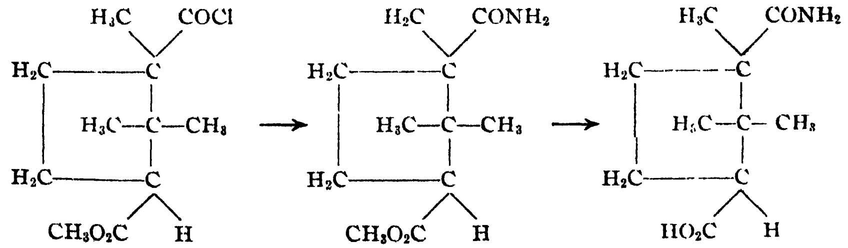
About 30% of the amino acid escaped decomposition.

The isomeric isoaminodihydrocampholytic acid has been prepared by Noyes and Knight[2] and its decomposition effected with nitrous acid. The study of the resulting products was far from complete, however. It was the aim of the present research to prepare the same compound, and investigate more completely the decomposition products formed with nitrous acid.

The isoaminodihydrocampholytic acid was prepared by the method of Noyes and Knight with some modifications. This method is indicated by the following:



d-Camphoric acid. *l*-Isocamphoric acid. α-Monomethyl ester of isocamphoric acid.[3]



β-Chloride of α-monomethyl isocamphoric ester. β-Amide of α-monomethyl isocamphoric ester. β-Isocamphoramidic acid.

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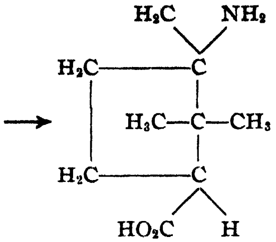
[1] This Journal, 34, 1073.

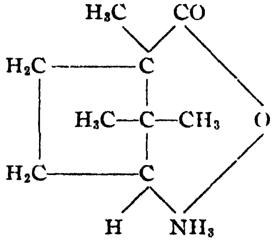
[2] *Ibid.*, 32, 1670.

[3] The secondary carboxyl is designated as α, the tertiary as β.



Isoaminodihydrocampholytic acid.

Free isoaminodihydrocampholytic acid was found to have a specific rotation, $[\alpha]_D^{21°} = -39.9°$, and for its hydrochloride, $[\alpha]_D^{19°} = -45.0°$. Both have the same sign of rotation. This is also true of aminodihydrocampholytic acid, ($[\alpha]_D = +54.7°$) and its hydrochloride ($[\alpha]_D = +41.3°$). For aminocamphonanic acid the reverse is true; for the free acid $[\alpha]_D = -29.2°$, and for its hydrochloride, $[\alpha]_D = +25.0°$. According to a view expressed by Noyes and Potter,[1] this indicates that aminocamphonanic acid forms an inner salt, thus:



while aminodihydrocampholytic acid does not. According to this view isoaminodihydrocampholytic acid does not form an inner salt in solution. This is to be expected from the fact that it is a *trans* compound. However, an intermolecular salt formation is indicated by an abnormally high molecular weight.

Decomposition of isoaminodihydrocampholytic acid with nitrous acid yields the following:

A hydrocarbon.	small amount
d-Campholytic acid.	35.8%
l-Campholytolacton.	4.2%
l-*Trans*-hydroxydihydrocampholytic acid (impure).	19.1%

The formation of *d*-campholytic acid in the decomposition furnishes the first direct evidence that it is the secondary asymmetric carbon atom of *d*-camphoric acid that rearranges to form *l*-isocamphoric acid, and fully establishes this accepted view. The experimental evidence on this point thus far has been that Walker and Wood[2] by the electrolysis of the potassium salt of tertiary ethyl isocamphoric ester obtained the same product as in the electrolysis of the corresponding camphoric ester. Aschan,[1] who did not consider this evidence conclusive because the compounds prepared by Walker and Wood were evidently impure, obtained *l*-isocamphoric acid as well as *d*-camphoric acid by the reduction of bromocamphoric anhydride, which points to the same view.

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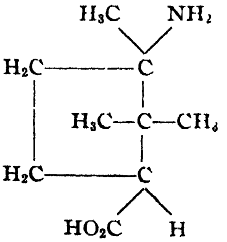
[1] Unpublished.

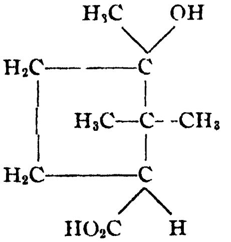
[2] *J. Chem. Soc.*, 77, 387 (1900).

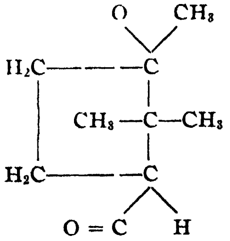
On the basis of Walker's results with campholytic acid, which led him to think that acid nearly or quite inactive, Aschan argues,[2] however, that the rearrangement occurs at the tertiary carbon atom. The fact, which had already been established by Noyes and Phillips,[3] but which had, apparently, been overlooked by Aschan, that campholytic acid has a high rotatory power, deprives this argument of its force. So far as we know, no one has discussed the question since Aschan's papers appeared. He considered the question as still open.

The hydroxy acid formed in this decomposition was regarded by Noyes and Knight as a *cis* compound, and they considered its formation as anomalous. Later it was shown[4] that the *d*-isomer was a *trans* acid. Hence this acid is *l*-*trans*-hydroxydihydrocampholytic acid and no inversion occurs in its formation above. In spite of this, the amount of the hydroxy acid formed is much less than the amount formed by inversion from the isomeric amino acid. On the other hand, the amount of the campholytic acid formed is very much greater.

The structure and identity of *l*-campholytolactone were established from a comparison with the properties of *d*-campholytolactone. It can be formed from isoaminodihydrocampholytic acid only by a partial Walden inversion. These relations can be better understood from the following formulas:


Isoaminodihydrocampholytic acid.


l-*Trans*-hydroxydihydrocampholytic acid.


l-Campholytolactone.

In the decomposition of isoaminodihydrocampholytic acid the Walden inversion occurs to a very small extent, 1.8%, while in the decomposition of dihydroaminocampholytic acid it takes place to a much larger extent,

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[1] *Ann.*, 316, 227 (1901).

[2] *Loc. cit.*

[3] *Am. Chem J.*, 24, 291 (1900).

[4] Noyes and Potter, *Loc. cit.*

45%. Since the iso-acid is a *trans* acid, and the aminodihydrocampholytic acid is a *cis* acid, and since the *trans* greatly exceeds the *cis* decomposition product in both cases, it is evident that the factor of "favored configuration" has an influence in the Walden inversion as encountered here.[1]

Experimental.

Preparation of l-Isocamphoric Acid.—Both the method of Marsh[2] and the method of Aschan[3] as modified by Noyes and Littleton[4] were tried. The latter method proved to be more satisfactory. It was carried out as follows: Eight sealed tubes each containing 100 grams of purified *d*-camphoric acid, 50 cc. of glacial acetic acid, and 5 cc. of hydrochloric acid (1.19) were heated in a bomb furnace at 175–180° for ten hours. Upon cooling, the viscous contents of the tubes were treated with three or four volumes of water. The mass was stirred frequently and in a half hour the greater part had crystallized. It was allowed to stand an hour longer, and was then filtered off. After drying on the water bath the pulverized material was thoroughly mixed with one-fourth its weight of acetyl chloride and allowed to stand for an hour. A quantity of water was added and the product filtered in order to remove the hydrochloric acid. The resulting mixture of *l*-isocamphoric acid and camphoric anhydride was separated by treatment with sodium bicarbonate solution. The isocamphoric acid was reprecipitated from the sodium bicarbonate solution and purified by dissolving in the smallest possible quantity of hot alcohol and reprecipitating by adding a quantity of hot water. The recovered anhydride was used in the next run. The yield of isocamphoric acid was one-third of the weight of camphoric acid used. As the anhydride was used again, no loss of material resulted.

Preparation of the α-Monomethyl Ester of Isocamphoric Acid.—The method of Noyes and Knight[5] was used to prepare this ester. The conditions, however, were more accurately regulated A solution of 100 grams of pure *l*-isocamphoric acid in 400 cc. of acetone-free methyl alcohol was heated to boiling in the water bath. Forty cc. of concentrated sulfuric acid were then added and the boiling continued for a half hour. The excess of methyl alcohol was rapidly distilled off under diminished pressure. The sirup-like residue solidified on the addition of water. The solid mass was filtered off and dissolved in sodium bicarbonate solution. The solution was extracted with ether to remove the diethyl ester, and the acid ester reprecipitated by the addition of hydrochloric acid. The raw product was recrystallized from petroleum ether (b. p. = 65–66°). The product melted at 88°. 100 grams of isocamphoric acid gave 80 grams of the pure acid ester.

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[1] See Noyes and Potter, THIS JOURNAL, **34**, 1070 (1912).

[2] *Chemical News*, **60**, 307.

[3] *Ber.*, **27**, 205.

[4] THIS JOURNAL, **35**, 77.

[5] *Loc. cit.*

Preparation of the β-Amido-α-methyl Isocamphoric Ester.[1]—The use of an indifferent solvent in preparing the chloride in the following method was suggested by the work of Haller[2] and of Bredt:[3]

To 20 grams of powdered phosphorus pentachloride, covered with 75 cc. of ligroin (b. p. 25-40°), 20 grams of α-monomethyl isocamphoric ester were added, and the mixture allowed to stand until the reaction was complete. The reaction flasks were provided with return condensers and the contents protected from the atmosphere with calcium chloride. Two or three hours were required for complete action. A clear solution finally resulted.

The chloride was not isolated, the ligroin solution being used directly to prepare the amide. The above solution was added dropwise to 100 cc. of ammonia water (sp. gr. = 0.90) which was cooled in a freezing mixture and stirred vigorously with a mechanical stirrer. The amide precipitated out during this process and was filtered off After drying on the water bath the raw product gave a melting point of 157°. Recrystallization by dissolving in a small amount of alcohol and reprecipitating with water did not change this melting point but removed a small amount of ammonium chloride present in the raw material. Twenty grams of acid ester gave 16 grams of the amide ester.

Saponification of the Amide Ester.—The method given by Noyes and Knight[4] for the saponification of the amide ester, yielded, on acidifying the saponified product, an amorphous, putty-like mass that did not become crystalline, even on standing for a week. This product was afterward found to contain 6 to 10% of *d*-camphoric imide.

With the following modified method, however, a crystalline product was obtained. Thirty grams of β-amido-α-monomethyl isocamphoric ester were dissolved in 75 cc. of 95% alcohol. 1.1 mol of 30% sodium hydroxide solution was added, and the mixture allowed to stand on the water bath over night. The alcohol was distilled off under diminished pressure. The viscous residue was dissolved in 75 cc. of water and carbon dioxide passed into this solution for an hour. 1.7 grams of *d*-camphoric imide precipitated and was filtered out. This was identified by its melting point, 244°, which remained unchanged when it was mixed with some of the imide prepared in another manner and by the specific rotation, $[\alpha]_D = 8.9°$ in a 10% solution in absolute alcohol, the specific rotation of the other imide being 8.1°.

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[1] The secondary carbon atom is designated by α, and the tertiary carbon atom by β

[2] *Bull. soc. chim.*, **70**, 984 (1896).

[3] *Ber.*, **45**, 1424.

[4] THIS JOURNAL, **32**, 1671.

On acidifying the filtrate from the imide, there was precipitated an amorphous mass that quickly became crystalline. After drying, the melting point was 160°. After one recrystallization from dilute alcohol it melted at 165°.

The β-amido-α-monomethyl isocamphoric ester was tested for *d*-camphoric imide, but none was found. The imide was therefore formed during the saponification. Its formation involves, of course, the shifting of the carboxyl group from the *trans* to the *cis* side of the ring with reference to the tertiary carboxyl and the shifting of a hydrogen atom in the opposite direction.

Preparation of the Hydrochloride of Isoaminodihydrocampholytic Acid.—19.9 grams of the β-isocamphoramidic acid were dissolved in 100 cc. of 10% sodium hydroxide. To this solution there were added slowly 140 cc. of a 10% sodium hydroxide solution into which 5.1 cc. of bromine had recently been aspirated. The temperature rose to 45°. When the temperature began to fall the solution was put on the water bath and kept at 75° for a half hour. After cooling, 1 cc. excess of hydrochloric acid (1.1) was added, and the solution evaporated to a small volume under reduced pressure. One mol of hydrochloric acid (1.19) was added and the hydrochloride separated from the sodium chloride by fractional recrystallization. Two recrystallizations from water gave a fairly pure product. Yield, 23 grams. A pure product was obtained by dissolving in absolute alcohol and precipitating with ether.

Found, 17 28% Cl; Calculated for $C_8H_{14}(CO_2H)NH_2HCl$, 17.09%.

One gram dissolved in 10 cc. of water gave a specific rotation $[\alpha]_D^{19°}$ = —45.8

The chloride melts at 296-298° with decomposition.

Isoaminodihydrocampholytic Acid.—The hydrochloride was exactly neutralized with sodium hydroxide and the free acid precipitated by adding a large excess of acetone. By precipitating this product twice from water solution with acetone a pure product melting at 235–236° was obtained. Noyes and Knight[1] found 225–227° for an impure product.

One gram of the acid in 10 cc. of water gave a specific rotation, $[\alpha]_D^{21°}$ = —32.9°.

Two molecular-weight determinations by the equilibrium method gave the following:

	Wt. of solution.	Wt. of acid.	T_F.	M(found).	M(theory).
I.	23.292 grams	1.0151 gram	0.439°	192	171
II.	19.151 grams	1.2741 grams	0.692°	190	. . .

The amphoteric nature of the substance evidently caused association in solution.

The Anhydride of Isoaminodihydrocampholytic Acid.—Distillation of the hydrochloride with lime does not yield an anhydride.[1] Heating a mixture of the hydrochloride, fused sodium acetate, and acetic anhydride for forty minutes with a free flame yielded an anhydride that was identical with the anhydride of aminodihydrocampholytic acid. Less vigorous conditions gave no anhydride.

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[1] *Loc. cit.*

The specific rotation found for the anhydride was, $[\alpha]_D = +74.2°$; 1 gram in 10 cc. of absolute alcohol. That of the anhydride prepared from *d*-aminodihydrocampholytic acid was +73.2°. The melting point was 191°, that of the anhydride from *d*-aminodihydrocampholytic acid was 188°, while the mixture melted at 189°.

The formation of the anhydride involves the shifting of the secondary carboxyl group from the *trans* to the *cis* side of the ring with respect to the amino group. This is in marked contrast to *d*-transhydroxydihydrocampholytic acid, which forms a *trans* lactone without shifting of the carboxyl group.[2] It seems a little remarkable that heating with acetic anhydride at a temperature below 150° should cause this rearrangement when heating with lime at a much higher temperature does not do so.

Decomposition of Isoaminodihydrocampholytic Acid with Nitrous Acid.—51.7 grams (0.25 mol) of the hydrochloride of isoaminodihydrocampholytic acid were dissolved in 150 cc. of water. 22.5 grams of solid sodium nitrite were added to the solution and the mixture kept at 10° for an hour. At the end of this time decomposition had nearly ceased. Three cc. of sulfuric acid (sp. gr. = 1.3) were then added and the whole allowed to come to room temperature. One cc. excess of 30% sodium hydroxide solution was added and 75 cc. of distillate distilled with steam to remove the hydrocarbon. The residue was acidified and extracted with ether. Upon evaporating the ether a thick sirup remained. This residue was distilled with steam until the distillate became clear. The distillate was extracted with ether. Evaporation of the ether gave a yellowish, oily residue consisting of an unsaturated acid and a lactone.

The unsaturated acid and lactone were separated by means of potassium carbonate solution. The weight of the lactone was 1.8 gram, that of the unsaturated acid, 15.4 grams.

The residue from the steam distillation consisted of a brown tar which contained the hydroxy acid and weighed 8.2 grams.

Purification of the Lactone.—The lactone was crystallized twice from petroleum ether. It was a white, waxy substance melting at 114–115°. Further recrystallization did not change the melting point. A sample of pure *d*-campholytolactone melting at 114–115° was mixed with this lactone, and the mixture melted at 114–115°, 0.8528 gram of the lactone dissolved in 10 cc. of absolute alcohol gave a specific rotation $[\alpha]_D$ = —8.2°. *d*-Campholytolactone has a specific rotation, $[\alpha]_D^{24°}$ = +8.5°. This shows the new lactone to be *l*-campholytolactone.

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[1] Both aminodihydrocampholytic acid and the chloride of aminocamphonanic acid ("aminolauronic acid"), which are *cis*-compounds, give an anhydride by this treatment. *Am. Chem. J.*, 16, 504, 507.

[2] Noyes and Potter, THIS JOURNAL, 34, 1074 (1912).

Hydrolysis of l-Campholytolactone; l-cis-Hydroxydihydrocampholytic Acid.—Seven tenths of a gram of *l*-campholytolactone and 2 cc. of 10% sodium hydroxide solution (1.25 mol) were heated on the water bath for three hours. The solution was acidified with hydrochloric acid and allowed to stand over night. Long, needle-like crystals were deposited. These were purified by dissolving in ether and reprecipitating by the addition of petroleum ether. The substance was an acid melting at 117–118°. It was mixed with a sample of *d-cis*-hydroxydihydrocampholytic acid, and the mixture melted at 117-118°. 0.3352 gram in 10 cc. of absolute alcohol gave a specific rotation, $[\alpha]_D$ = —53.1°. *d-cis*-Hydroxydihydrocampholytic acid has a specific rotation, $[\alpha]_D$ = 50.8° and a melting point of 118.5°. The acid obtained by hydrolysis of *l*-campholytolactone is therefore *l-cis*-hydroxydihydrocampholytic acid.

The formation of this lactone and acid involves a shifting of the methyl and hydroxyl groups each to the opposite sides of the ring while the carboxyl group, and hydrogen atom retain their positions. This is in marked contrast with the conduct of the amino acid given above.

Purification of the d-Campholytic Acid.— The unsaturated acid obtained from the nitrous acid decomposition above was fractionally distilled with steam. The first fraction gave the highest specific rotation, $[\alpha]_D^{26°}$ = +66.35°. Its density was 1.006 at 25°/25°. *l*-Campholytic acid has a specific rotation, $[\alpha]_D$ = —70.0[1] and its density is 1.010. The new unsaturated acid is consequently *d*-campholytic acid.

As a further proof of its identity the acid was analyzed.

Calculated for $C_8H_{13}COOH$· C, 70 09; H, 9.16.
Found: C, 70.13; H, 9.34.

0.7633 gram required 9.98 cc. of half-normal alkali for naturalization as against 9.91 cc. for the theory.

Preparation of Racemic Campholytic Acid.—Two-tenths of a gram each of *l*- and *d*-campholytic acid were mixed. On standing at —17° for an hour the mixture solidified. The product dried on a porous plate melted at 31–32°. By recrystallizing from petroleum ether to constant melting point it melted at 37.8°. A similarly purified sample of *r*-campholytic acid prepared from inactive camphor melted at 40.5°. A mixture of the two melted at 38.0°. The identity of the unsaturated acid was thus established beyond question.

d-Trans-hydroxydihydrocampholytic Acid.—The tarry hydroxy acid crystallized with great difficulty. Only a few crystals were obtained.

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[1] Noyes and Potter, THIS JOURNAL, 34, 1077 (1912).

These melted at 132°. Since this acid has already been fully characterized,[1] the experiment was not repeated.

The hydrocarbon was obtained in an amount too small for study, its presence being indicated by the odor. It was doubtless isolaurolene.

Summary.

In conclusion the results of this investigation may be stated as follows:

1. The method of preparing isoaminodihydrocampholytic acid has been improved.

2. The free acid and the hydrochloride have been studied. The physical constants have been determined. A trans anhydride is not formed when the hydrochloride is heated with acetic anhydride and sodium acetate, but a rearrangement occurs to form the anhydride of the isomeric-*d*-aminodihydrocampholytic acid.

3. Decomposition of isoaminodihydrocampholytic acid with nitrous acid yields a hydrocarbon, *d*-campholytic acid, and *l*-*trans*-hydroxydihydrocampholytic acid. The Walden inversion occurs to only a slight extent in this decomposition, owing, probably, to a favored configuration.

4. A direct proof of the relation of *l*-isocamphoric acid to *d*-camphoric acid has been obtained.

URBANA, ILLINOIS

THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS.

[SECOND PAPER.]

BY MAITLAND C BOSWELL

Received October 20, 1913

A direct method for the determination of oxygen in organic compounds was described in the first paper of this series.[2] In the case of compounds of high oxygen content this gives satisfactory results, but if the oxygen is less than 30 40%, depending on the nature of the compound, the results are too high. In some cases, as anthraquinone, the results exceed the true value to the extent of several per cent., owing to the formation of reaction products other than water and carbon dioxide, which condense in the absorption apparatus. The method can hence be used with security only in the case of compounds containing at least 40% of oxygen. The present paper describes a method applicable to compounds, irrespective of the amount of oxygen present in them. It consists in heating a weighed quantity of substance in a quartz combustion tube in a current of nitrogen, causing the vapors to pass over a small quantity of heated copper oxide of known oxidizing value distributed over a long layer of asbestos, weighing the water and carbon dioxide formed, and determining the oxidizing value of the copper oxide remaining unreduced. The copper is then oxidized in the tube without disturbance, under definite conditions, by a current of oxygen, and is again ready for another determination.

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[1] Noyes and Knight, *Loc. cit.*

[2] *J. Am. Chem. Soc.*, 35, 284 (1913).

Let x grams = oxygen in weighed amount of substance.
Let a grams = total oxygen available from the copper oxide in the tube.
Let b grams = oxygen available from the copper oxide remaining after the combustion.
Let c grams = oxygen in the water formed.
Let d grams = oxygen in the carbon dioxide formed.
Then $x + a = b + c + d$.
$x = b + c + d - a$.

The hydrogen content of the substance is also calculated from the weight of water formed.

In this method two possible difficulties and sources of error are at once apparent. Will the vapors of the substance be completely burned by the necessarily small amount of copper oxide used, and is it possible to so oxidize the copper and reduce the resulting copper oxide that a constant quantity of oxygen is available for each analysis? By a measurement of the rate of oxidation of the copper and of the reduction of the copper oxide, it was found that both of these processes, after proceeding for a definite determinable time, continue at velocities so small that it is practicable to obtain a definite amount of copper oxide, of definite available oxygen content, by allowing oxidation and reduction to proceed for definite intervals of time, and that an error as great as five minutes in timing makes no appreciable difference in the oxygen available. No difficulty was experienced in effecting complete combustion of the vapors distilling from the substance. As the boat containing the substance is heated finally to a white heat, no oxygen compound can remain undecomposed.

Description of Apparatus.—A quartz tube, 12 mm. internal diameter and 980 mm. long, is filled for a length of 570 mm. (starting 110 mm. from one end) with asbestos, which has been impregnated with a solution of approximately 4 grams of copper in nitric acid, by evaporating the solution and heating the residue until all the nitrate has been transformed into oxide. This leaves a space 300 mm. long at one end of the tube, which, during the analysis, is partly occupied by a quartz boat containing the substance. The tube rests in a combustion furnace of the usual form, except that the iron trough and tiling supporting the combustion tube are removed, so that in an analysis the whole of the oxide may be brought to a red heat before the substance has begun to distil. The nitrogen is made by carefully warming in an Erlenmeyer flask, a mixture of 75 grams sodium nitrite, 115 grams ammonium sulfate, 75 grams potassium bichromate and 225 cc. water. Heat is applied only to start the reaction. The evolution of nitrogen proceeds with rapidly increasing velocity,, owing to the heat of the reaction, and, unless controlled by immersion of the flask for a few seconds at a time in water and ice, may become explosive in violence. The gas holder containing the nitrogen is connected with a purifying apparatus, consisting of a quartz tube 360 mm. long containing a tight roll of copper gauze 130 mm. long, which is heated in a small gas furnace of two wide, flat flames. This removes any traces of oxygen in the gas. This is followed by a U-tube containing calcium chloride and two sulfuric acid washers of special form[1] which give very thorough contact of gas and acid with small friction and pressure head. The absorption apparatus which is attached to the other end of the tube, consists of a U-tube with bulb containing concentrated sulfuric acid on pumice, to absorb water, and a U-tube containing soda lime followed by a U containing sulfuric acid on pumice, for the determination of carbon dioxide.

Measurements were first made to determine the conditions of oxidation of the copper and reduction of the oxide in order that a constant amount of oxygen shall be available for each analysis. The details of this procedure will be given presently The following results were obtained:

	a	*b*	*c.*		*a*	*b.*	*c.*
1	—	5	0.9538	8	45	25	0.9235
2	—	90	..	9	45	30	0.9240
3	0	5	0.8116	10	90	30	0.9247
4	0	45	0.8168	11	90	40	0.9256
5	45	0	0.9170	12	90	30	0.9241
6	45	5	0.9198	13	90	40	0.9250
7	45	20	0.9226				

a is the time in minutes of heating of the copper in oxygen after the glow has ceased.

b is the time in minutes of the reduction with hydrogen after the hydrogen is running freely from the combustion tube.

c is the weight in grams of water formed.

All the copper at the outset is present as oxide. This is not true subsequently, for after reduction in hydrogen and oxidation of the copper, only a portion of the reduced copper is oxidized, the remainder being protected by the external layer of oxide, so that the velocity of oxidation becomes very slow. This is clearly shown in the above results, the amount of oxygen available from the original oxide (experiment 1) being greater than in any subsequent reduction. The results also indicate that the hydrogen penetrates the layer of oxide more effectively than the oxygen, for in 5 minutes (experiment 1) the hydrogen has removed more oxygen from the original oxide than a subsequent reduction (experiment 12) lasting 30 minutes, the oxidation prior to this last reduction having lasted 90 minutes. This indicates that it is first necessary to reduce the original oxide very thoroughly. This is accomplished by passing hydrogen over the heated oxide for 90 minutes. Experiments 8, 9 and 11 show that in 45 minutes the copper is almost as effectually oxidized as in 90 minutes, and experiments 9, 10 and 12 show that in 45 minutes the copper is almost as effectually oxidized as in 90 minutes. Experiments 8 and 9, 10 and 11, 12 and 13 show that, at the end of 25 minutes, the reduction is proceeding at such a low rate that in 5 minutes only 0.0005 gram of water are formed. Hence, if the copper is each time oxidized for 45 minutes and the oxide formed reduced for 30 minutes, a constant amount of oxygen will always be available. The rate of passage of the gases has probably no influence in either the oxidation or reduction, provided there is always an excess of gas present in both cases, and provided the velocity is sufficient to carry off the water vapor immediately it is formed, and thus prevent any equilibrium between copper, copper oxide, and water vapor. Although the temperature may have greater influence on the rates of oxidation and reduction, it is probable that, at the high temperature at which these are conducted, a considerable change of temperature would be necessary to seriously alter them. No special precautions were taken to secure either constant gas flow or constant temperature, beyond turning the furnace on fully in each operation. This, along with the direct play of the flames against the quartz tube, secured a very high temperature almost immediately.

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[1] *Trans. Faraday Soc.*, **6,** 10 (1910).

Method of Procedure.—0.2 gram of substance is weighed out in a quartz boat and inserted in the combustion tube about 60 mm. from the asbestos carrying the copper oxide. A rapid stream of nitrogen is sent through the tube for 20 minutes. The rate of nitrogen flow is considerably diminished, and the absorption tubes are attached. The whole layer of copper oxide is now heated to the highest temperature attainable in the furnace, and three burners lighted at the other end of the tube. The flow of nitrogen is further diminished to about 1 bubble per second, and the substance heated very gently. The rate of flow of gas in the purifying apparatus and also the absorption vessels is carefully observed, and at the first indication of either too rapid flow through the latter, or a diminution of rate through the former, due to a sudden generation of pressure in the combustion tube, the heating of the substance is discontinued until the normal rate is reëstablished. After all the burners have been turned on full, the heating is continued for 20 minutes longer, with a somewhat more rapid flow of nitrogen in order to sweep over all products of combustion. The absorption apparatus is disconnected, the contained nitrogen displaced by air, the end of the combustion tube is closed and the furnace allowed to cool. Another weighed U-tube, containing conc. sulfuric acid on pumice, is now connected to the tube and a rapid stream of purified hydrogen, generated electrolytically, by means of the apparatus described in the first paper. is caused to pass; the hydrogen generator being connected by a T tube to the same purifying apparatus used for the nitrogen. The flames are lighted two at a time, starting with those nearest the absorption tubes. The hydrogen is so rapidly oxidized that none escapes the action. When the bubbles commence again to pass through the absorption tube the next pair of burners is lighted. These operations are continued until all the copper oxide is heated and hydrogen is running freely through the tube. The rate of passage of hydrogen is now reduced somewhat, and the heating continued for 30 minutes longer. The U-tube is now detached, and the hydrogen displaced by air. The other absorption tubes from the first operation can be weighed during this 30-minute interval. In order to prepare the copper oxide for a second analysis, oxygen is passed through the tube, all the burners are lighted, and the oxidation continued for 45 minutes after the bright glow, which passes rapidly through the tube, ceases.

The following results were obtained in the analysis of carefully purified compounds:

	1.	2.	3.	4	5	6	7	8.	9.
Succinic acid.	0 2018	0.0825	0.1789	0 6687	0 1087	53 9	54.2	5.1	5.1
Cane sugar.	0.2020	0.0993	0 1051	0.7230	0.1060	52 5	51 5	6 1	6.4
Phthalic anhydride..	0.1658	0 0322	0 1398	0.7046	0.0552	33.3	32 4	2 4	2.7
α-Naphthol.............	0.1909	0.0797	0.2846	0.4775	0.0204	10 7	11 1	5 2	5 5

Column 1 gives the number of grams of substance taken.

Column 2 gives the number of grams of oxygen corresponding to the water formed in the combustion.

Column 3 gives the number of grams of oxygen corresponding to the carbon dioxide formed.

Column 4 gives the number of grams of oxygen corresponding to the water formed in the reduction of the copper oxide remaining.

Column 5 gives the number of grams of oxygen in the substance obtained by adding the corresponding weights in columns 2, 3 and 4 and subtracting 0.8214 gram, the total weight of oxygen available from all the copper oxide.

Column 6 gives the determined percentage of oxygen in the substance.

Column 7 gives the calculated percentage of oxygen in the substance.

Column 8 gives the percentage of hydrogen in the compound determined from the weight of water formed in the combustion, and corresponding to the oxygen given in column 2.

Column 9 gives the percentage of hydrogen in the compound calculated from the formula.

On comparing the results in columns 8 and 9, it is seen that the agreement of the hydrogen determined by the method, with the hydrogen calculated from the formulas, is about as close as that usually obtained in the ordinary carbon-hydrogen method. The oxygen percentages determined, given in column 6, differ from the calculated values, given in column 7, by amounts varying from 0.3% to 1%. In view of the indirectness of the oxygen determination a greater degree of accuracy could scarcely be expected.

Summary.

A method has been worked out for the simultaneous determination of hydrogen and oxygen in organic compounds, giving results differing by 0.3% from the calculated values in the case of hydrogen, and by 0.3% to 1% from the calculated values in the case of oxygen.

UNIVERSITY OF TORONTO.

[FROM THE LABORATORIES OF THE REFEREE BOARD OF CONSULTING SCIENTIFIC EXPERTS AT THE UNIVERSITY OF PENNSYLVANIA.]

A COPPER BALANCE ON SEVEN[1] EXPERIMENTAL SUBJECTS TO DETERMINE THE EFFECT OF EATING COPPERED VEGETABLES.

BY CARL L. A. SCHMIDT.

The following work constitutes part of the investigation on the "Action of Coppered Vegetables on the Health and Nutrition of Man" conducted under the general direction of Dr. A. E. Taylor of the Referee Board, the general results of which have appeared in Report No. 97 of the United States Department of Agriculture. Since Taylor's conclusions as to the harmfulness of the ingestion of vegetables colored with copper sulfate are almost entirely based on the fact that copper was apparently retained by the individuals eating coppered vegetables, it was thought important to publish the work in detail as a separate article.

The subjects, all of them medical students, were put on a constant diet previously determined by them in an experimental period. A certain amount of peas constituted a part of the daily menu for each individual. The diet was altered in some cases during the course of the experiment by substituting for part or all of the vegetables an increasing amount of peas or string beans so as to increase the amount of ingested copper. The coppered vegetables were purchased in large lots on the open market. For serving, the vegetable was steamed in the can, thrown on a colander, thoroughly mixed, and a sample taken for analysis at the same time that the portions were weighed out by the men. The experiment was divided into three parts—a foreperiod of two weeks during which time the men were given uncolored peas; an experimental period of nine weeks, during which coppered peas and string beans were eaten; and a two weeks' after- or controlperiod of uncolored peas and string beans. One subject was designated as control. He ate the same diet as the others, except, that uncolored peas and string beans were substituted for the coppered vegetables. For five days at the close of the experiment he was given copper sulfate in milk.

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[1] There were eight experimental subjects. Subject No. 1 was a poor subject for experimentation, being strongly influenced by psychological factors. For this reason the results obtained from him are omitted.

Urin was collected daily and determinations of nitrogen, phosphorus, and copper made. Feces were collected in aggregates of two- or three-week periods as indicated in Table I. Separation of the stools corresponding to the different periods was accomplished by giving charcoal on the morning of the new period. Feces from the afterperiod were collected in two lots of one week each so that the final week's collection might be free from any possible contamination of the stool from the previous period of coppered peas. In this way, a comparison between the normal output of copper in the final control week and the two weeks' foreperiod could be made. Feces were thoroughly dried and finely ground.

Copper in the vegetables and feces was estimated by the well-known method of electrolysis from a sulfuric acid solution, the copper being deposited on a platinum gauze electrode and subsequently weighed. One hundred grams of peas or string beans were thoroughly mixed with an excess of sulfuric acid in a porcelain dish, desiccated, and ignited at a low temperature. Addition of a few grams of potassium sulfate prevented any fusion. In determining copper in feces, 30 grams were ashed and an aliquot of the solution taken to represent 25 grams. The analytical factor for the daily input of copper varied between 1.5 and 3, since 100 grams of sample were taken for analysis, while the factor for the output averaged about twenty. The input of copper was determined daily, which might slightly increase the error for the total input. However, errors due to the daily sampling of the vegetable will probably equalize during a long time, while the error in the output copper was minimized by taking the average of several closely agreeing determinations. Estimation of the copper in the urins was carried out on five days' composit samples of 100 cc. each. The urin was oxidized by dropping into a heated mixture of nitric and sulfuric acids; the nitric acid then driven off by heating until white fumes appeared. All organic matter, except a small amount of an aromatic compound, is destroyed. This apparently resists oxidation; it can sometimes be noticed in the distillate from a Kjeldahl nitrogen determination. The sulfuric acid solution was electrolyzed, any traces of copper on the electrode dissolved with nitric acid and estimated colorimetrically as the ferrocyanide. Only faint traces of copper were found; the amount was never greater than that obtained on a blank determination. The elimination of copper in the urin is therefor excluded, a fact similarly observed by Long.[1]

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[1] J. H. Long, Report No. 97, United States Department of Agriculture, 1913, p. 423.

TABLE I.—INPUT AND OUTPUT OF COPPER. (GRAMS.)

Subject No. 8.

1911.	Input.	Output.	Balance.
Mar. 1–14	..	0.031	...
Mar. 15–Apr. 4	0.3555	0.274	...
Apr. 5–19	0.3262	0.351	...
Apr. 20–May 2	0.3183	0.292	...
May 3–16	0.4487	0.513	...
May 17–23	..	0.019	...
May 24–30	..	0.018	...
Total	1.449	1.498	—0.049

Subject No. 7.

1911.	Input.	Output.	Balance.
Mar. 1–14	..	0.026	...
Mar. 15–Apr. 4	0.3555	0.289	...
Apr. 5–19	0.3262	0.294	...
Apr. 20–May 2	0.3183	0.389	...
May 3–16	0.4809	0.454	...
May 17–23	..	0.043	...
May 24–30	.	0 019	...
Total	1.481	1.514	—0.033

Subject No. 2.

1911.	Input.	Output.	Balance
Mar. 1–14	..	0.037	...
Mar. 15–Apr. 4	0.3555	0.310	..
Apr. 5–18	0.2293	0.220	..
Apr. 19–May 2	0.1753	0.187	..
May 3–16	0.2737	0.294	...
May 17–23	..	0.018	.
May 24–30	..	0.015	..
Total	1.034	1.081	—0.047

Subject No. 6.

1911	Input.	Output.	Balance
Mar. 1–13	..	0.029	. .
Mar. 14–21	..	. .	..
Mar. 22–Apr 4	0 2337	0.175	...
Apr. 5–18	0.2293	0.248	...
Apr. 19–May 2	0.1753	0.258	...
May 3–16	0.2737	0.292	. .
May 17–23	..	0 022	..
May 24–30	.	0.015	..
Total	0.912	1.039	—0.127

Subject No. 5.

1911.	Input.	Output.	Balance.
Mar. 1–14	..	0.036	...
Mar. 15–Apr. 4	0.3555	0.314	...
Apr. 5–20	0.3262[1]	0 330	...
Apr. 21–25		...	...
Apr. 26–May 2	0.1758	0.190	...
May 3–16	0.4487	0.424	...
May 17–23	..	0.055	...
May 24–30	.	0.019	...
Total	1.306	1.368	—0.062

Subject No. 3.

1911.	Input.	Output.	Balance.
Mar. 1–14	..	0.028	..
Mar. 15–27	..	0.035	...
Mar. 28–Apr 11	0 2512	0.165	...
Apr. 12–25	0.1985	0 220	...
Apr 26–May 2	0.0880	0.100	...
May 3–16	0.2737	0.215	...
May 17–23	..	0.016	...
May 24–30	..	0.018	...
Total	0.811	0.797	+0.014

Subject No. 4.

1911.	Input.	Output.	Balance.
Mar. 1–14	...	0.016	...
Mar. 15–Apr. 4	...	0.047	...
Apr. 5–18	...	0.027	...
Apr. 19–May 2	...	0.057	...
May 3–16	...	0.041	...
May 17–23	0.157[2]	0.125	...
May 24–30	...	0.014	...
Total	0.157	0.327	—0.170

[1] No peas eaten on Apr. 20.

[2] 0.0314 gram Cu as $CuSO_4$ in milk for 5 days.

TABLE II.—RÉSUMÉ.

Actual copper balances.

A.

Period of eating vegetable colored with $CuSO_4$.	Subject No. 8. M. W.	Subject No. 7. J. F. W.	Subject No. 2 M. R. B.	Subject No 6 W. C. T.	Subject No. 5. C. P. K.	Subject No. 3 O. H. C.	Subject No. 4. E. S. F.
Input of Cu in vegetable, grams	1.449	1.481	1.034	0.912	1.306	0.811	0 157[1]
Other input of copper, gram. . .	0.140	0.117	0.167	0.125	0.148	0 100	0.016
Total input of copper, grams. . .	1.589	1.598	1.201	1.037	1.454	0.911	0.173
Total output of copper, grams.	1.430	1 426	1.011	0.973	1.258	0.700	0.125
Retention of copper, gram . .	0 159	0 172	0.190	0.064	0.196	0.211	0.048

B.

Entire time of experiment.	Subject No 8 M W.	Subject No. 7 J F. W.	Subject No 2. M. R. B.	Subject No. 6. W. C. T.	Subject No 5. C. P K.	Subject No 3 O. H. C.	Subject No 4. E S F.
Input of Cu in vegetable, grams	1.449	1 481	1.034	0 912	1 306	0.811	0.157
Other input of copper, gram . .	0 202	0.169	0 241	0.185	0.219	0.182	0.204[2]
Total input of copper, grams....	1 651	1 650	1 275	1.097	1.525	0.993	0.361
Total output of copper, grams	1.498	1 514	1.081	1.039	1.368	0 797	0.327
Retention of copper, gram. . . .	0.153	0.136	0.194	0 058	0.157	0.196	0.034

Table I shows the input of copper, the output in the different periods, and the corresponding balances, as well as the grand totals for the entire time of the experiment. It will be seen at once that during the foreperiod there was an output of copper in the feces of all subjects, although apparently no copper was given. This can only be accounted for by the fact that small amounts of copper were present in the foods eaten. That many cereals and vegetable products contain small traces of copper has been shown by other observers.[3] All subjects including the control showed an output of copper during the foreperiod, the amounts being nearly the same in all cases. If some of the feces of the second period had been carried over into the first, one would naturally expect that the amounts would vary; similarly some of the first period's feces would, in some subjects, be carried over into the second period, in which case either no copper ought to appear in those feces (*i. e.*, if there was no copper normally ingested in foods) or only that resulting as normal elimination. The amount of copper normally ingested was too small for direct estimation. The average daily ingested matter (including water) for subject No. 8 for the two weeks of foreperiod was 3070 grams. During that time the output copper in the feces was 0.031 gram. This would allow less than 1 mg. of copper per kilo of ingested matter.

The analytical balances of all subjects, except No. 3, are negative as shown in Table I. A small retention is observed in No. 3. In order that a true balance may be obtained, an allowance must be made for normally ingested copper. This can be done by assuming that the output during the foreperiod corresponds to the normal input during that time. That this assumption is very nearly correct is shown by the fact that the average daily elimination of copper in the final control week of all subjects corresponds very closely to that of the two weeks of foreperiod.

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[1] Balance for week when $CuSO_4$ was taken in milk.

[2] Calculated from entire time subject was control.

[3] *Ibid.*, page 214 and 424.

Taking the output of copper in the foreperiod of each subject as the basis of normal input copper, we can arrive at a balance which probably represents more nearly the true copper balance. Part A of Table II shows the copper balance during the period when vegetables colored with copper sulfate were eaten, allowances being made for a normal input of copper, while part B of the same table shows the balance for the entire time of the experiment. All subjects show a plus balance. This clearly indicates a retention of copper.

The plus balances obtained cannot be wholly due to analytical error, since it is not conceivable that the analytical error, which is largely due to sampling, should always be in the same direction for the entire time of the experiment. It may also be said that during the course of the experiment the diet was changed by substituting for part or all of the vegetables, coppered peas and string beans, and hence the normal input of copper as calculated from the foreperiod is incorrect. This is true only to slight extent since the amount of vegetables daily ingested is small as compared to the total of other ingested matter. The figures, as given, may not show the absolute copper balance, but since in all the subjects the balance is decidedly positive and of the same order of magnitude, the only conclusion is that there was a retention of copper in all individuals. That there was a retention even after the two weeks of afterperiod is also shown. That the copper so retained will probably be held in the body for some time and but slowly eliminated, is indicated by the fact that the average daily elimination of copper in the final control week is nearly the same for all subjects as that of the two weeks foreperiod.

Conclusions.

(1) Seven subjects on an experimental diet, a part of which consisted of coppered vegetables, showed a distinct retention of copper.

(2) In order to obtain a true balance, an allowance must be made for copper normally ingested in foods. This value can be obtained by assuming that the output of copper in the foreperiod represents the copper ingested during that time.

(3) The copper so retained in the body will probably be only slowly eliminated.

Board of Health,
Berkeley, California

[FROM THE LABORATORIES OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND OF JEFFERSON MEDICAL COLLEGE.]

FASTING STUDIES. XII. THE AMMONIA, PHOSPHATE, CHLORIDE AND ACID EXCRETION OF A FASTING MAN.

BY D. W. WILSON AND P B. HAWK.

Received October 15, 1913.

Numerous investigations have been made on fasting men and a large amount of valuable information has been collected, though few attempts have been made to correlate the excretion of the substances we wish to consider.

Benedict,[1] in his masterly fasting studies, determined the excretion of phosphates and chlorides. The phosphate output increased to a maximum on the first to fourth day of the fast in various experiments. In general, the chloride excretion was considerable for the first two days, with a marked decrease on the third day. Thereafter, the elimination tended to diminish, but with considerable variation. It was also observed that, where the volume of ingested water was over 1000 cc., the volume of urine was not far from that of the water consumed.

Cathcart,[2] in his work on Beauté, showed an increased excretion of ammonia during the fast, which reached a maximum on the eighth day of the fourteen-day fast and decreased thereafter. The acidity and phosphate output ran parallel, reaching a maximum on the third day and diminishing gradually during the remainder of the fast. The chloride excretion decreased steadily. The amount excreted of all four constituents dropped suddenly to a minimum value, during the starch and cream diet fed subsequent to the fast, and increased toward the normal upon the return to the original high protein diet which was fed previous to the fast. There was a retention of 10 to 11 grams of chlorides.

Van Hoogenhuyze and Verploegh[3] determined the acidity, phosphate and chloride output in a fasting experiment on Tosca. The acidity reached a maximum on the third day of the fast while the phosphate excretion was highest on the fourth. Thereafter there was a general, though irregular, decrease in the output of both constituents. As in Cathcart's experiment, their excretion diminished immediately when food was given. The chloride output decreased suddenly on the first day of the fast and showed marked fluctuations throughout, with the minimum values near the middle of the fast.

Experiments on Succi, in which he fasted thirty days for Luciani[4] and twenty-one days for Ajello and Solaro,[5] show the acidity and phosphate output running parallel, with a maximum on the fifth day followed by a gradual decrease. The chloride excretion gradually diminished with considerable oscillation. There was a marked retention of phosphates and chlorides during the first feeding days after the latter fast. During the last ten days of the former fast, sugar, gelatine and peptone were fed.

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[1] *Carnegie Publication*, No. 77 (1907).

[2] *Biochem. Z.*, 6, 109 (1907).

[3] *Z. phys. Chem.*, 46, 440 (1906).

[4] *Das Hungern., Leipzig* (1890).

[5] *La Riforma Medica*, 9, [2] 542 (1893).

E. and O. Freund[1] report another twenty-one day fast on Succi, in which the acidity increased on the second day and decreased thereafter, while the phosphate excretion was highest on the first day and diminished throughout the fast. The ammonia output decreased during the first three days, then rose to a maximum and diminished to a low value during the remainder of the experiment.

Lehmann, Müller, Munk, Senator and Zuntz[2] publish results of experiments on Cetti, fasting ten days, and Breithaupt, fasting six days. In both cases, the acidity and phosphate output rose to a maximum on the third day and decreased steadily thereafter. The chloride excretion, in the former case, rose to a maximum on the second day and decreased during the remainder of the fast, while in the latter experiment it diminished steadily throughout.

Brugsch[3] determined the various constituents excreted in the last seven days of a thirty-day fast of Succi. He found a high ammonia output (35% of total nitrogen), the chloride and phosphate excretion low, but fairly constant, and the acidity diminishing.

Hoover and Sollman[4] report a case of fasting during hypnotic sleep, in which the phosphate excretion increased to a maximum on the final day and the chloride output decreased to about half its original value during the fast.

Description.

The purpose of this experiment was to determine, if possible, any relations between the ammonia, phosphate, chloride and acid excretion by way of the urine during a seven-day fast and during subsequent low and high protein feeding periods.

The subject (E) was a man weighing 76.6 kilograms at the beginning of the fast and 71.4 kilograms at the end of the period of inanition. He was an instructor in the Chemistry Department of the University of Illinois and had previously[5] been a subject in a fasting experiment of similar length carried out at that university. During the fast, he kept up his daily routine of work as instructor.

The diet, described in a previous paper,[6] for the preliminary and final periods, consisted of 600 grams graham crackers, 1350 grams whole milk, 75 grams butter, 150 grams peanut butter, 1050 cc. water (300 cc. at meal time and 750 cc. between meals). This diet contained 21.86 grams of nitrogen (136 grams protein) with an energy value of about 6000 calories, which gave the subject 1.77 grams protein and 80 calories per kilogram of body weight. The fast was seven days in length, with a daily water ingestion of 1500 cc. Following the fast, was a low-protein period of four days during which 5.23 grams nitrogen or about one-fourth of the regular diet was ingested daily. The subject also received 1500 cc. water daily. The diet for the final period was the same as that for the preliminary period.

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[1] *Wiener klin. Rundschau*, **15**, 69, 91 (1901).

[2] *Virchow's Archiv.*, **131**, supplement (1893).

[3] *Zeit. exp. Path. Ther.*, **1**, 419 (1905).

[4] *J. Exp. Med.*, **2**, 405 (1897)

[5] Howe, Mattill and Hawk, *J. Am. Chem. Soc.*, **33**, 568 (1911).

[6] Sherwin and Hawk, *J. Biol. Chem.*, **11**, 169 (1912).

The urine was collected in twenty-four-hour periods and kept in a refrigerator in two-liter acid bottles. Thymol was used as a preservative.

The methods of analysis were as follows: ammonia, Folin; total acidity, Folin; phosphates, uranium acetate titration; chlorides, Clark's modification of Dehn's method.

Experimental.

Preliminary Feeding Period.—The subject was placed on a uniform diet which contained 21.86 grams nitrogen per day. The preliminary feeding period lasted four days, during which a satisfactory nitrogen equilibrium was maintained. The urine and the various constituents under consideration were excreted in fairly constant amounts and furnish a normal average for comparison. The ammonia output was noticeably low.

Fasting Period.—During the fast, the subject continued his regular activities as instructor. The amount of water taken daily was 1500 cc. The urine volume was low on the first day, rose on the second, and remained fairly constant with a slight decrease toward the end of the fast. The average was nearly the same as that of the preliminary period.

The ammonia excretion (see table and curves accompanying) increased on the first day of the fast and rose rapidly at first, and then slower, reaching a maximum on the sixth day of 1.463 grams nitrogen, over eight times the average of the preliminary period. On the last day of the fast the value dropped to 1.394 grams.

The acid output rose immediately on the first day of the fast, more than doubled itself on the second day and was still higher on the third. Thereafter, there was a gradual decrease to the end of the fast.

The phosphate excretion increased slightly on the first day, dropped on the second, but reached a maximum on the third. After the third day, the values decreased steadily.

The chloride excretion was less than normal at the outset of the fast and decreased rapidly for three days, after which time there was a slower and less steady diminution.

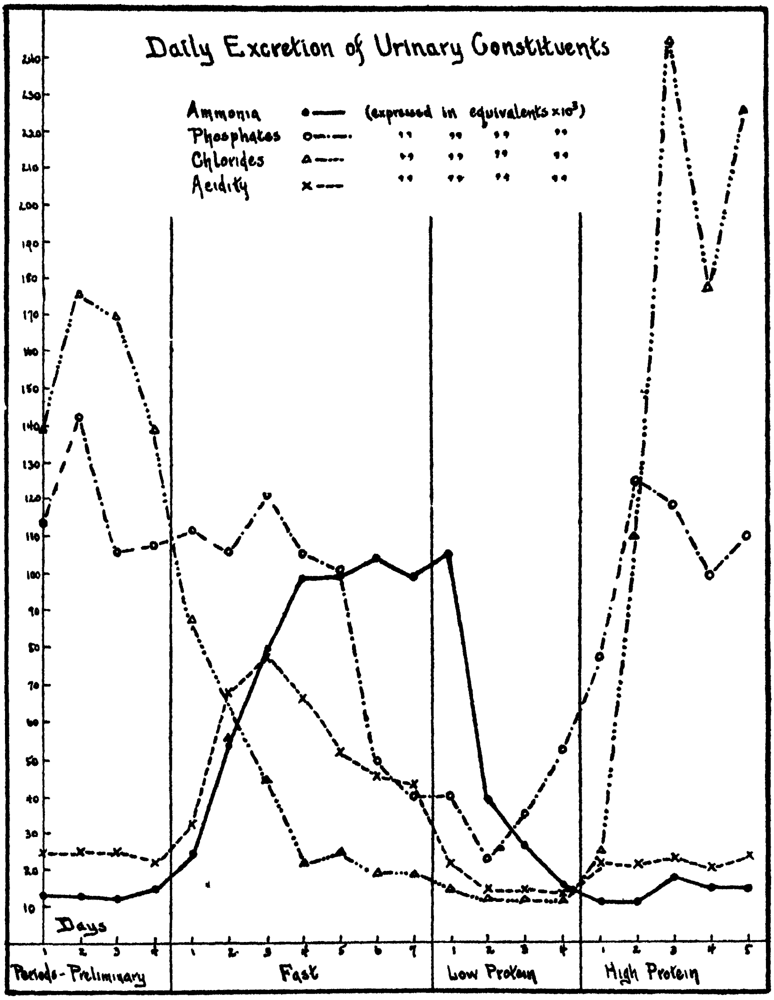
GENERAL DATA.

Subject E.

Day of Exp.	Vol. urine. Cc.	Ammonia N. Grams.	Acidity. Cc. $N/10$ NaOH.	P_2O_5. Grams.	Chloride. Grams. NaCl.	NH_3 % total N.	$\frac{P_2O_5}{\text{Acidity}}$
			Preliminary Period.				
1.........	1200	0.185	245.2	2.683	7.996	1.05	0.109
2.........	1350	0.177	245.2	3.358	10.232	1.00	0.137
3.........	1210	0.158	246.7	2.503	9.801	0.89	0.101
4.........	1150	0.209	217.2	2.527	8.000	1.18	0.116
Av.....	1228	0.182	238.6	2.768	9.007	...	0.116
			Fasting Period.				
1.........	990	0.344	328.9	2.616	5.035	2.39	0.079
2.........	1345	0.747	677.1	2.509	3.231	4.21	0.037
3.........	1540	1.113	770.4	2.851	2.539	5.70	0.037
4.........	1340	1.388	664.2	2.490	1.253	8.62	0.037
5.........	1410	1.390	525.0	2.376	1.474	10.46	0.045
6.........	1015	1.463	462.4	1.186	1.132	11.22	0.026
7.........	1120	1.394	438.9	0.955	1.137	10.98	0.022
Av.....	1251	1.120	552.4	2.140	2.257	...	0.040
			Low-Protein Final Period				
1.........	900	1.479	214.8	0.951	0.874	13.19	0.044
2.........	1000	0.552	140.6	0.537	0.714	6.40	0.038
3.........	1240	0.370	143.4	0.822	0.710	4.54	0.057
4.........	1330	0.217	136.2	1.246	0.762	2.51	0.091
Av.....	1118	0.655	158.8	0.889	0.765	...	0.058
			High-Protein Final Period.				
1.........	970	0.161	212.0	1.830	1.404	1.14	0.086
2.........	1420	0.158	205.5	2.934	6.322	1.04	0.142
3.........	2530	0.241	228.0	2.778	14.063	1.73	0.122
4.........	1550	0.207	199.6	2.332	10.220	1.49	0.117
5.........	2175	0.204	228.7	2.587	13.029	1.29	0.113
Av.....	1729	0.194	214.8	2.492	9.008	...	0.116

Low Protein Feeding Period.—At the close of the fasting period, the subject was placed on a diet similar to that of the preliminary period but only one-fourth that amount, so that, for four days after the fast, the subject received 5.23 grams nitrogen and about 1800 calories daily. The urine volume was low on the first day but increased gradually giving an average a little below normal for the period.

The ammonia nitrogen was higher on the first day of the low protein feeding period than on the last day of the fast and was, indeed, slightly higher than the maximum value for the fast. A marked decrease was observed on the second day, the value dropping from 1.479 grams to 0.552 gram with a continued decrease each day following. The minimum



value, however, was somewhat higher than any value in the preliminary period.

The acidity dropped immediately after the fast to a value lower than any observed in the preliminary period, and decreased further giving a minimum value for the experiment on the fourth day. The excretion of phosphates diminished slightly on the first day and showed a considerable decrease on the second, after which there was a steady and rapid increase to a value about half that of the preliminary period. The chloride excretion dropped considerably on the first day and decreased somewhat on the next and stayed about this minimum value for the remainder of the period.

Final Period.—The final period consisted of five days, during which the food intake was increased to the amount eaten in the preliminary period. The urine volume was again low on the first day but rose rapidly to a maximum value on the third day, and then decreased to a value above the normal. The average was considerably above that of the preliminary period.

The ammonia output continued to decrease for the first two days, but showed a marked rise on the third from 0.158 gram to 0.241 gram, an increase of over 52%. On the fourth and fifth days, the values were decreased to somewhat above the average of the preliminary period.

The acid output increased on the first day of the final period to a value somewhat below the normal, and showed no great variation throughout the period.

The phosphate excretion increased rapidly, giving values on the second and third days above the normal. For the remainder of the period, the output was somewhat below the average of the preliminary period.

The output of chlorides rose rapidly for the first three days of the final period, and reached a maximum of 14 grams on the third day. The values for the last three days showed considerable variation and were all higher than the average of the preliminary period.

General Discussion.

The urine volumes varied within normal limits throughout the experiment. There was, however, a considerable diminution on the first day of each period (see Table p. 140). The volumes were less than a liter on these days only. In each case, there was a marked retention of water; for the daily water intake (water + water in milk) was 2225 cc. for the preliminary and final periods, 1500 cc. for the fast, and 1890 cc. for the low-protein period. The uniformly observed decrease in the urine volume on the first day of each period is remarkable owing to the difference in the conditions of the experiment at these times, but may indicate a retention due to a change in the metabolic activities of the body both on beginning and discontinuing the fast. A similar retention occurred in the previous fast on this subject.[1] On the first day of that fast, with an intake of 1000 cc. water, the excretion was only 678 cc., and on the first two days following the fast, with water ingestions of 1000 cc. and 1750 cc., the excretions were 507 cc. and 527 cc., respectively. Uniform weather conditions precluded the possibility of great variations in loss of water by other channels than the kidneys.

On the third day of the fast, the urine volume was 1540 cc., which was 40 cc. more than the water intake. This was the only time during the fast when the volume of liquid excreted was larger than the volume ingested. Our data, in this respect, are comparable with Benedict's[2] observation that, when the volume of ingested liquid exceeds 1000 cc., the urine volume is not far from that of the liquid ingested. The average urine volume was higher for the fast than for the preliminary period.

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[1] Howe, Mattill and Hawk, THIS JOURNAL, 33, 568 (1911).

[2] *Carnegie Publication*, No. 77 (1907).

In the low protein period, there was a steady increase from the minimum on the first day. The volumes in the final period increased daily from the minimum on the first day to the maximum for the experiment on the third day, when the volume of urine was again greater than that of the ingested liquids.

The ammonia output rose immediately on the first day of the fast and increased rapidly, both absolutely and relatively, to a maximum value on the sixth day, which was eight times the average for the preliminary period (see Table p. 140). There was a slight decrease on the seventh day. The relative ammonia values increased in like manner from 1% of the total nitrogen in the preliminary period to 11% on the sixth day. A similar increase occurred in the former fast by this same subject, giving in that instance a value of nearly 13% on the seventh fasting day.[1] These results are similar to those reported by Cathcart, in which he found an increase to 15% of the total nitrogen on the eighth day of the fast. In striking contrast, E. and O. Freund in their work on Succi found scarcely any increase in the ammonia excretion.

Our ammonia nitrogen value rose to 13% on the first day of the low protein period and decreased steadily throughout the period. Cathcart feeding a nitrogen-free diet observed a marked increase in three days from 7% to 11% of the total nitrogen. In both our investigation and that of Cathcart the relative value was near the normal in the final period.

This increased elimination of ammonia during the fast has been frequently observed by various investigators and explained as due to acidosis, caused by the formation of the acid products of fat metabolism. In fasting, the body must draw on its own stores of glycogen and fat for energy and, as the fat is metabolized, the acid products formed, diacetic and β-hydroxybutyric acids, accumulate so rapidly that a condition of acidosis is established which calls for an increased formation of ammonia to aid in maintaining the normal reaction of the body fluids. In this consideration, it is interesting to compare the figures we have obtained for ammonia, acidity and phosphate, as excreted in the urine during and following the fast. An inspection of the curves in the figure will make the relations clearer.

The values of the three constituents just mentioned were increased at the beginning of the fast. The ammonia output rose rapidly to a maximum on the sixth day; the acidity increased to a maximum on the third day and then gradually decreased; the phosphate output increased in general to the third day and then decreased, the relative decrease being closely parallel to that of the acidity. Cathcart,[1] Van Hoogenhuyze and Verploegh,[2] Benedict,[3] Luciani,[4] Ajello and Solaro,[5] Munk[6] and others report somewhat similar results for the constituents which they determined.

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[1] Howe, Mattill and Hawk, THIS JOURNAL, 33, 568 (1911).

The explanation of the relations above mentioned may lie in the complicated mechanism by which the body attempts to maintain a uniform reaction of its fluids. As soon as fasting starts, the glycogen and fat stores of the body are called upon to furnish the necessary energy for the body. At first, the glycogen is used in large amounts, the fats being called upon more and more as the fast progresses. Thus, on the first day, the acids formed by fat metabolism were produced in small amounts only, which called for but a slight increase in the ammonia formation and a slightly increased acid and phosphate output.

Henderson's work[7] on the relation of phosphate to the maintenance of neutrality of the body fluids shows that they play an extremely important role. As acids are formed in the body and pass into the blood or lymph, an equilibrium is immediately established, some of the di-sodium phosphate present changing to monosodium phosphate. An excess of monosodium phosphate in the blood is excreted by the kidneys, due either to an increased tendency to dialyze as shown by Maly,[8] or to a function of the kidneys, or both. Thus, an increased phosphate excretion with increased urine acidity follows an increased formation of acids in the body. Just such a condition was met with in our experiment. The acids formed by fat metabolism caused increased excretion of phosphates with increased urine acidity.

After the glycogen stores were depleted, the fat metabolism became more marked, as shown by a greater increase in the ammonia output on the second day, when the excretion was more than doubled. The ammonia formation did not, however, keep pace with the acid formation as indicated by the increased acidity of the urine on the second day of the fast. The relatively low value of the phosphate output is unexplained. The third day showed an increased excretion of all three constituents. Thereafter, the ammonia increased, but the acidity and phosphate output decreased, indicating that the production of ammonia had caught up with the acid production within the body and was gradually exceeding it. With the increase of ammonia, there would be a smaller amount of free acids to be eliminated and therefore a decreased urine acidity. The ammonia excretion reached a maximum on the sixth day and decreased on the seventh, which may have been caused by decreased fat metabolism, due to a lessening of the fat stores of the body.

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[1] *Biochem. Z.*, 6, 109 (1907).

[2] *Z. Physiol. Chem.*, 46, 440 (1906).

[3] *Carnegie Publication*, No. 77 (1907).

[4] *Das Hungern.*, *Leipzig* (1890).

[5] *La Riforma Medica*, 9, [2] 542 (1893).

[6] *Virchow's Archiv.*, 131, supplement (1893).

[7] Henderson, *J. Biol. Chem.*, 9, 403 (1911). Fitz, Alsberg and Henderson, *Am. J. Physiol.*, 18, 113 (1907).

[8] *Ber.*, 9, 164 (1876).

At the beginning of the fast, there was a marked decrease in the ratio of phosphates to acidity, indicating that less than usual of the urinary acidity was due to acid phosphates. The ratio decreased to a lower figure as the fast progressed, which may be accounted for by the rapid increase of acidosis in the body and the increased excretion of free organic acids in the urine. This explanation is confirmed by the fact that β-hydroxybutyric and diacetic acids were present in considerable amounts during the last days of the fast, when the phosphate-acidity ratio was at its minimum value. Undoubtedly, also, a deficiency of phosphates, caused by their continuous excretion, was instrumental in bringing about a retention which continued through practically all of the low protein period.

With the intake of food, the ratio of phosphates to acidity increased quickly, due to a decreased excretion of organic acids as indicated by a comparison of values for the first and third days of low protein ingestion. These show a decreased phosphate excretion, accompanied by an increase in the ratio of phosphates to acidity. The ratio swung to a value above normal on the second day of high protein feeding and then returned to a normal figure, indicating that the body fluids had returned to their usual condition of equilibrium where the monosodium phosphate excreted is the chief factor causing urinary acidity.

On the first day of the low-protein feeding period, the ammonia output increased considerably, exceeding slightly the maximum value of the fast. This may have been due to an attempt of the organism to reduce the acidosis of the body. As a result of this high ammonia formation, the acidity dropped to less than half the value of the previous day. This decrease in acidity was undoubtedly also accentuated by the ingestion of food, which furnished bases for neutralization of acid metabolic products and calories which alleviated the condition of acidosis.

The diet of the low-protein period seemed sufficient to overcome much of the acidosis, as the ammonia output decreased nearly two-thirds on the second day and diminished thereafter to the end of the period. The acidity of the urine decreased in general with a slight increase on the third day. The phosphate output diminished nearly one-half on the second day, and increased slowly to the end of the period. This retention of phosphates has been noted by Cathcart, Benedict, and Van Hoogenhuyze and Verploegh, and may indicate a tendency on the part of the body to regain its normal amount of phosphates. The ratio of phosphates to acidity increased toward the normal.

With the high-protein ingestion, there was an immediate decrease in the ammonia excretion. The output of the first two days was rather below the normal average, but on the third day the excretion increased more than 50% with a return to slightly above normal for the remainder of the period. The high value on the third day has been noted before in experiments,[1] in this laboratory, on this and two other subjects[2] and in certain other data, especially in Cathcart's work on Beauté. In the latter experiment, a slight rise occurred on the third day of normal feeding following two days of non-nitrogenous food ingestion. This rise in the ammonia following fasting has been explained in a previous article, by one of us,[2] as due to an attempt on the part of the body to free itself of the last traces of acidosis so that it may return to a normal metabolic régime. This explanation gains support from the fact that on this day there was also a high excretion of acids and phosphates.

The increase in the ammonia output on the third day after the fast, as mentioned above, was less in our present experiment on Subject E than in the previous experiment, made upon this same subject. In the former instance he passed immediately to a high protein diet at the conclusion of the fast, whereas in this instance he was on a low protein diet for four days before ingesting the high protein diet. The difference in the dietary conditions and the added fact that the organism may conduct itself differently metabolically in a repeated fast[2] may account for the variation noted.

By examining the data for the low-protein period, we note that no increase occurred but, instead, a continuous decrease. The non-appearance of the rise in the ammonia excretion on the third day of this period may have been due to the fact that the food ingested, being but one-fourth the amount of the normal diet, was low not only in nitrogen but also in calorific value and the body was still forced to derive a part of its energy from its own fat supply, thus allowing a continued, though decreased, formation of acids from fat metabolism and a continued state of acidosis.

The chloride output throughout the experiment seemed to bear no relation to the excretion of the other constituents considered. It decreased rapidly during the first four days of the fast and remained fairly constant for the remainder of the period with a slight diminution. In the low-protein feeding period, the excretion dropped to less than one-tenth of the normal output, showing a considerable retention. A similar retention has been observed in a number of experiments as previously noted.

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[1] Howe, Mattill and Hawk, THIS JOURNAL, 33, 568 (1911).

[2] Howe and Hawk, *Ibid.*, 33, 215 (1911).

[FROM THE LABORATORIES OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND OF JEFFERSON MEDICAL COLLEGE.]

FASTING STUDIES. XIII. THE OUTPUT OF FECAL BACTERIA AS INFLUENCED BY FASTING AND BY LOW AND HIGH PROTEIN INTAKE.

BY N. R. BLATHERWICK AND P. B. HAWK.

Received November 12 1913.

So far as we are aware, the influence which fasting exerts upon the output of fecal bacteria has not been studied. Schmidt and Strasburger[1] state that during fasting the output of dry bacteria is one and one-third gram per day. No data are submitted. The amount of fecal bacteria excreted per day during a fast should, of course, decrease because of the withdrawal of food and the consequent absence of the products of the digestion of such food from the contents of the intestine However, one would not expect a complete cessation of bacterial growth, inasmuch as albuminous secretions continue to be poured into the lumen of the intestine even during a fasting interval.[2]

The course of intestinal putrefaction as measured by the urinary indican excretion has been followed in a few cases. One of the first experiments of this sort was that made by Müller[3] upon the professional faster Cetti. He found no indican in the urine after the third day of fasting. The procedures for the detection of indican were not fully developed at that time. One would naturally expect to find indican in the urine of a fasting individual because of the fact mentioned above, that secretions and juices containing protein material are poured into the intestine even during periods of inanition. Baumstark and Mohr[4] also report the absence of indican in the urine of a fasting dog after the elimination of the "hunger feces." In our experience, fasting feces continue to be passed throughout a fasting interval of over 100 days.[5] Experiments made in our laboratory have also shown a pronounced decrease in the indican output of a 76 kilogram man during a seven-day period of inanition.[6]

Description.

Data as to subject, diet and experimental periods are given in a previous paper.[7] A description of methods is also given in another connection.[8]

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[1] "Die Fäces des Menschen," p. 286.

[2] Mosenthal, *Proc. Soc. Exp. Biol. Med*, **8**, 40 (1910)

[3] *Berl. klin. Woch.*, **24**, 433 (1887); also *Virchow's Arch*, p. 133, supplement (1893).

[4] *Z. exp. Path. Ther.*, **3**, 687 (1906).

[5] Howe, Mattill and Hawk, *J. Biol. Chem*, **11**, 103 (1912).

[6] Sherwin and Hawk, *J. Biol. Chem.*, **11**, 169 (1912)

[7] Wilson and Hawk, THIS JOURNAL, **36**, 137 (1914).

[8] Blatherwick and Hawk, *Biochemical Bulletin*, **3**, No. 9, 1913.

Discussion of Results.

During the preliminary period of four days (21.86 grams of nitrogen per day), the average daily excretion of fecal nitrogen was 2.815 grams (see Table I). Of this amount 1.571 grams or 55.82% was bacterial nitrogen. The actual excretion of bacteria was 14.34 grams per day, constituting 34.03% of the dry feces.

Table I.

Subject E—Fast.

Stool No.	Weight of stool. Grams.	% dry matter.	Wt. dry matter. Grams.	Fecal N. Grams.	Bacterial N. Grams.	Bact. dry matter. Grams	% dry bact. in dry feces. Grams.	Bact. N. in fecal N %.
			Preliminary Period (4 Days).					
1	97.0	22.23	21.56	1.412	0.752	6.861	31.82	53.26
2	166.0	22.65	37.60	2.368	1.351	12.327	32.78	57.05
3	184.5	23.34	42.94	2 891	1.513	13.805	32.15	52.33
4	215.0	22.31	47.96	3.081	1.747	15.940	33.24	56.70
5	35.5	26.55	9.43	0.614	0.379	3.458	36.69	61.73
6	31.0	29.12	9.03	0.893	0.543	4.954	54.88	60.81
Total	729.0	...	168.52	11.259	6.285	57.345	...	...
Average	182.3	23.12	42.13	2.815	1.571	14.336	34.03	55.82
			Fasting Period (7 Days).					
1	81.0	11.34	9.185	1.504	0.352	3.212	34.97	23.40
2	38.5	19.47	7.495	0.682	0.354	3.230	43.10	51.91
Total	119.5	...	16.68	2.186	0.706	6.442	...	...
Average	17.1	13.99	2.38	0.312	0.101	0.920	38.62	32.29
			Low Protein (4 Days).					
1	44.0	18.28	8.043	0 633	0.358	3.266	40.61	56.55
2	19.0	8.98	1.706	0.143	0.075	0.684	40.09	46.05
Total	63.0	...	9.75	0.776	0.433	3.950	...	...
Average	15.75	15.48	2.44	0.194	0.108	0.988	40.51	55.80
			High Protein (5 Days).					
1	192.5	21.61	41.59	2.779	1.564	14.270	34.31	56.28
2	230.0	14.76	33.94	2.210	0.944	8.613	25 38	42.71
3	86.5	19.95	17.25	1.127	0.589	5.374	31.15	52.26
4	135.0	22.60	30.51	2.014	1.114	10.164	33.31	55.31
5	180.5	22.79	41.13	2.659	1.549	14.133	34.36	58.25
6	48.5	25.44	12.34	0.820	0.490	4.471	36 23	59.76
Total	873.0	...	176.76	11.609	6.250	57.025	...	...
Average	174.6	20.25	35.35	2 322	1.25	11.405	32.26	53.84

The feces of the fasting period were quite readily separated from those of the other periods because of the different character of the stools. Neither carmine nor charcoal was utilized in making the separation. The feces passed during the fasting interval (2 stools) were more fluid in character and darker in color than the feces resulting from the cracker-milk diet of the feeding periods. The fasting feces when examined macroscopically apparently consisted principally of mucous and residues of secretions. Microscopical examination demonstrated large numbers of bacteria.

The bacterial suspension, however, had a much different appearance than did that of the stools passed during feeding. After adding the alcohol the supernatant liquid assumed a reddish green tinge in contrast to the customary brown color seen in such suspensions. When the bacterial substance had settled it also possessed a greenish tinge. Bile may have been a contributing factor in this color variation.

The weight of fecal nitrogen excreted per day during the fast was 0.312 gram, of which 0.101 gram or 32.29% was of bacterial origin. The actual output of dry bacteria per day was but 0.92 gram, a most marked decrease from the daily value of 14.34 grams observed during the preliminary feeding interval.

Following the fast, the subject was fed a low-protein (5.23 grams of nitrogen per day) diet for a period of four days. Two stools were collected during this interval. The amount of fecal nitrogen excreted daily was 0.194 gram, of which 0.108 or 55.80% was of bacterial origin. The average daily excretion of dry bacteria was 0.988 gram or 40.51% of the total fecal (dry) output.

The original high-protein diet of the preliminary period was now resumed. The average weight of fecal nitrogen passed per day during this five-day period was 2.322 grams. Of this total excretion 55.84% or 1.250 grams was bacterial nitrogen. The actual output of bacterial substance was 11.405 grams or 32.26% of the dry feces.

When the four parts of the experiment are compared, the variations in the bacterial data are very striking. The amount of bacterial dry substance excreted per day, for example, was 14.336 grams during the preliminary period, 0.92 gram for the fast, 0.988 gram for the period of low-protein ingestion and 11.405 grams for the final high-protein period. Similar variations were observed in the bacterial nitrogen values. The very marked decrease in bacterial values during the fasting interval was expected because of the absence of food digestion products in the lower intestine. That the bacterial output for the low protein period was about the same as that for the fasting interval is significant. That there was no greater bacterial development when 5.23 grams of nitrogen were daily introduced into the body than when *no nitrogen* was introduced may be taken as evidence of very thorough utilization of the food nitrogen, thus leaving no extra pabulum for the microörganisms. The fact that the fecal nitrogen values, both total and bacterial, were not so great during the final period as during the preliminary period, although an identical diet was ingested in each instance, may also be taken as evidence of a better utilization of the protein constituents of the diet following the fast. Undoubtedly the need of nitrogen to make good the tissue destroyed during the fast played an important part in producing the better food utilization.

It will be noted that the percentage of dry bacteria in dry feces was increased during the fasting and low-protein periods. This was to be expected, since the ingestion of large amounts of protein (21.86 grams of nitrogen) would increase the amount of undigested and indigestible residues, while the increase of bacteria would not be relatively as great.

It is interesting to note that the feces passed during fasting contain smaller numbers of bacteria per day than during a period of normal feeding, but that the fasting feces contain a larger relative proportion of bacteria than do feces passed during such an interval of feeding.

Bacteria versus Indican.—In the appended table (II) will be found a comparison of the data for the excretion of fecal bacteria and urinary indican by the subject of the present investigation. The indican values are taken from data reported by Sherwin and Hawk.[1]

TABLE II.—RELATIONSHIP OF FECAL BACTERIAL NITROGEN TO URINARY INDICAN OUTPUT.

	Experimental period			
Constituent determined	Preliminary.	Fasting.	Low-protein.	High-protein.
	Excretion per day			
Indican (mgs.)	48.9	32.9	74 1	79 6
Bacterial nitrogen (grams)	1.571	0.101	0 108	1 250

It will be noted that the indican values are very high for the low-protein period following the fast. This phenomenon is difficult of explanation. If this high indican value is to be interpreted as being due to increased putrefaction, brought about by less complete absorption of protein from the intestine, it would be logical to expect that the total nitrogen of the feces would be proportionately increased. However, our fecal nitrogen data (Table I) show no such increase. The daily output of fecal nitrogen for the preliminary period was 2.815 grams, whereas the daily output for the period of low-protein ingestion subsequent to the fast was but 0.194 gram. In other words, the ratio between the nitrogen of the diets was as 4 : 1 while the ratio between the resultant fecal nitrogen values was as 14.5 : 1. It is apparent, therefore, that instead of being relatively increased, the nitrogen in the feces has undergone a very pronounced *relative decrease*. This finding of itself, considered apart from all associated factors, might be interpreted as indicative of a much more satisfactory absorption during the period of low-protein ingestion, subsequent to the fast.

Another surprising observation in this connection is the fact that the actual average daily output of bacteria during the low-protein feeding period was only about $^1/_{14}$ as great as during the preliminary interval. That increased putrefaction should come coincidently with a decrease in the bacteria value to approximately $^1/_{14}$ of the original, is certainly a surprising observation. What factors may have been instrumental in bringing about such a condition of affairs? In the first place it is entirely possible that the intestinal flora before the fast, although highly developed as was indicated by an average daily output approximating 14 grams, was nevertheless made up in large part of non-indole-forming bacteria. They may, in turn, have been relatively inactive in so far as the actual formation of indole was concerned. Under such conditions then, we would have a low indole output from an intestinal flora which was copious in quantity. A condition such as this could, of course, be brought about by proper manipulation of the diet.[1] In the experiments from this laboratory under consideration, however, the conditions were such as to lead one to expect a pronounced intestinal putrefaction at the very point where the low indican value was obtained, *i. e.*, on the high-protein diet. We could further cite, from the data thus far obtained from experimentation upon subject E in this and other connections, facts which seem to indicate that there is, of necessity, no uniform relationship between the urinary indican excretion and the fecal bacteria output under a similar dietary régime.

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[1] Sherwin and Hawk, *J. Biol. Chem.*, 11, 169 (1912).

During the fast it is possible that certain indole-forming organisms formed a progressively increasing proportion of the intestinal flora due to their greater resistance to the rigors of the fasting régime. Therefore, at the end of the fast, although there was an actual reduction in the mass of the flora, these indole-formers may have made up the major portion. Unhampered by the presence and activities of other types of microorganisms these active indole-organisms were able to bring about a very rapid formation of indole and the stimulated absorptive mechanism caused this indole to be very completely absorbed and rapidly put through the subsequent detoxicating process which yielded the urinary indican. These factors may have played an important part in the peculiar relationship which we note between fecal bacteria and urinary indican output.

Conclusions.

By means of a seven-day fast the daily excretion of fecal bacterial nitrogen by a 76 kilogram man (E) was reduced from 1.571 grams to 0.101 gram, whereas the actual weight of the excreted bacterial substance was reduced from 14.336 grams to 0.920 gram per day. The percentage of the fecal nitrogen which was present as bacterial nitrogen was decreased from 55.82% to 32.29% as a result of the fast. The percentage of dry bacteria in dry feces was slightly increased.

The output of bacterial nitrogen and the output of bacterial substance were approximately the same on a low-protein diet as during fasting. With the ingestion of a high-protein diet these values underwent an immediate and pronounced increase.

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[1] Kendall, *J. Med. Res.*, **29**, 411 (1911).

The percentage of the fecal nitrogen which was composed of bacterial nitrogen was about the same in the periods of low- and high-protein ingestion.

There was no definite relationship between the excretion of fecal bacteria and that of urinary indican.

The ingestion of 5.23 grams of nitrogen *after* the fast was followed by an excretion of fecal bacteria which was only $^1/_{14}$ as great as when four times that amount of nitrogen was ingested *before* the fast.

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[FROM THE LABORATORIES OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND OF JEFFERSON MEDICAL COLLEGE.]

STUDIES ON WATER DRINKING. XVI. THE INFLUENCE OF DISTILLED WATER DRINKING WITH MEALS UPON FAT AND CARBOHYDRATE UTILIZATION.

BY N. R. BLATHERWICK AND P. B. HAWK.

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So far as we are aware, the only study of the utilization of fat and carbohydrate, as influenced by the ingestion of large volumes of water at meal time, is that reported by Mattill and Hawk.[1] In the tests cited in that report the subjects were young men and the water employed was a freshly prepared *softened* water. A somewhat better utilization was secured when large volumes of water were taken with meals. The variations, however, were not very marked except in the case of the fat utilization by one subject. In this case, the percentage utilization was increased from 94.3% to 96.5% as a result of high water intake.

The statement is frequently made that distilled water ingestion, because of the absence of electrolytes in such water, has a harmful influence upon the animal body. In this connection, Findlay[2] says that the ingestion of distilled water is followed by the swelling of the surface layers of the gastric epithelium and that "salts also pass out, and the cells may die and be cast off. This may lead to catarrh of the stomach." Harlow[3] and Koeppe[4] also believe that catarrh of the stomach may follow the ingestion of distilled water (iced). Nocht[5] and Winkler[6] report experiments which failed to demonstrate that any bad effect followed the drinking of distilled water. Spitta[7] believes that we have, as yet, no definite solution to the problem as to whether the ingestion of distilled water is followed by harmful influences. Oehler,[1] on the other hand, has recently reported tests on white mice, which seem to indicate that the drinking of distilled water brought about hemoglobinuria. It is well established that the introduction of distilled water into the blood stream will bring about a hemoglobinuria of a transient character, but we are rather skeptical as to the possibility of *ingested* distilled water producing any such disorder. We are investigating this feature of the water drinking problem.

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[1] *J. Am. Chem. Soc.*, 33, 1978 (1911).

[2] "Physical Chemistry and its Applications in Medical and Biological Science," London, 1905.

[3] Quoted by Oehler.

[4] *Deut. med. Wochschr.*, 1898, 624

[5] *Hyg. Rundschau.*, 1892, 273.

[6] *Z. physikal. diat. Ther.*, 8, 671 (1905).

[7] "Rubner's Handbuch Hygiene," Leipzig, 1911, 28.

Description.

A complete description of the general plan of this series of experiments upon distilled water drinking with meals has been reported in a recent paper.[2] This experiment comprised three periods; (*a*) a preliminary period; (*b*) a copious water period, and (*c*) a final period. A uniform diet was maintained throughout the experiment.

The method used for the fat determinations was that of Kumagawa and Suto[3] with the modification proposed by Inaba.[4] In the determination of carbohydrates in the feces, a modification of Strasburger's method[5] was employed. The method was exactly the same as that used in the former work by Mattill and Hawk,[6] except that the reducing power of the solution was determined by Benedict's new quantitative method.[7]

The diet contained 155.4 grams of fat and 293.2 grams of carbohydrate per day, distributed among the various dietary constituents as indicated in Table I.

TABLE I.—COMPOSITION OF DAILY DIET.

Food.		Fat.		Carbohydrate	
Dietary constituent	Amount Grams	%.	Amount. Grams	%.	Amount. Grams
Milk............	1200	4.0	48.0	5.71	68.5
Graham crackers....	300	7.8	23.4	72.5	217.5
Butter...........	75	84.4	63.3	negligible	
Peanut butter.......	45	46.0	20.7	16.0	7.2
Total...........	..	..	155.4	.	293.2

Discussion of Results.

Fat Utilization—Subject C.—During the preliminary period, an average of 6 grams of fat was excreted daily (see Table II). The % of fat in the moist feces was 8.4. Water ingestion caused a decrease in these values.

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[1] *Münch. med. Woch.*, **59**, 50 (1912).

[2] Blatherwick and Hawk, *Biochemical Bulletin*, **3**, No. 9, 1913.

[3] *Biochem. Z.*, **8**, 213 (1908).

[4] *Ibid.*, **8**, 348 (1908).

[5] *Die Fäces des Menschen*, p. 173.

[6] THIS JOURNAL, **33**, 1978 (1911).

[7] *J. Am. Med. Assoc.*, **57**, 1193 (1911).

The data indicate that, during the water period, the feces contained a lower percentage of fat (8.21%) and that there was a lower output of fat per day (5.54 grams). The final period, in which the original dietary conditions obtained, showed 5.47 grams of fat excreted daily; the percentage of fat in the stools being still further reduced to 7.64%. The percentage utilization of fat during the three periods was 96.14, 96.43 and 96.50%, respectively. Water apparently caused a slightly better utilization of the ingested fat. However, the variations are within normal limits for utilization values.

TABLE II.—FAT EXCRETION—SUBJECT C.

Stool No.	Weight of stool.	Weight of dry matter.	Per cent. fat in fresh feces.	Weight of fat.
	Preliminary Period (5 Days).			
1	43.5	10.19	8.23	3.58
2	43.5	11.60	8.25	3.59
3	60.5	18.37	8.94	5.41
4	73.5	21.87	8.05	5.92
5	136.0	37.66	8.46	11.51
Total	357.0	99.69	.	30.01
Average	71.4	19.94	8.40	6.00
	Copious Water (5 Days).			
6	57.5	13.67	9.33	5.36
7	43.5	12.91	8.02	3.49
8	56.5	14.46	7.96	4.50
9	86.5	24.44	7.65	6.62
10	93.5	26.85	8.27	7.73
Total	337.5	92.33	..	27.70
Average	67.5	18.47	8.21	5.54
	Final Period (5 Days).			
11	72.0	19.58	7.07	5.09
12	66.5	18.07	8.27	5.50
13	72.5	18.25	7.61	5.52
14	74.5	17.28	7.34	5.47
15	72.5	16.44	7.98	5.79
Total	358.0	89.62	..	27.37
Average	71.6	17.92	7.64	5.47

Subject V.—The daily output of fat during the preliminary period was 6.06 grams, 4.89% of the stools being composed of fat (see Table III). Under the influence of water, these values became 6.36 grams and 6.80%, respectively. In the final period, the daily excretion of fat was 5.04 grams and the percentage value 4.52. These values are considerably lower than those obtained in the preliminary period before the high water ingestion, and also lower than those of the water period. It is probable that the ingestion of the large volume of water stimulated the activities concerned in fat utilization, but that the influence of the water was not felt at once but became slightly apparent in the after period. If we combine the water period and final period we find that during this ten-day interval the average daily fat lost by feces was 5.70 grams. This is an appreciable drop from the output of 6.06 grams per day, which we secured in the preliminary period. The utilization values for the three periods are 96.15%, 96.00% and 96.82%, respectively. The utilization value for the ten-day interval beginning with the water ingestion is 96.39%. Here, again, it may be considered that the variations in the utilization values fall within normal limits.

TABLE III.—FAT EXCRETION—SUBJECT V.

Stool No.	Weight of stool.	Weight of dry matter.	Per cent. fat in fresh feces.	Weight of fat.
	Preliminary Period (5 Days).			
1	48.5	10.17	5.57	2.70
2	56.5	13.65	6.51	3.68
3	244.5	47.09	4.97	12.16
4	154.5	27.19	4.54	7.01
5	115.5	22.23	4.11	4.75
Total	619.5	120.33	.	30.30
Average	123.9	24.07	4.89	6.06
	Copious Water (5 Days).			
6	56.0	10.65	5.42	2.94
7	75.5	16.90	6.73	5.08
8	44.5	7.05	7.06	3.14
9	120.0	26.75	7.03	8.43
10	171.5	38.60	7.12	12.21
Total	467.5	99.95	..	31.80
Average	93.5	19.99	6.80	6.36
	Final Period (5 Days).			
11	162.5	32.97	4.98	8.10
12	124.5	23.89	4.63	5.76
13	56.5	11.90	4.27	2.41
14	214.0	34.52	4.17	8.92
Total	557.5	103.28	..	25.19
Average	111.5	20.66	4.52	5.04

Carbohydrate Utilization—Subject C.—The daily output of carbohydrate during the preliminary period was 1.39 grams (see Table IV). Under the influence of distilled water ingestion this value became 1.29 grams, whereas the value for the final period was 1.13 grams. The percentage utilization was practically the same for each period, the actual figures being 99.52%, 99.56% and 99.62%, respectively for the three periods of the experiment.

TABLE IV.—CARBOHYDRATE EXCRETION—SUBJECT C.

Stool No.	Weight of stool.	Weight of dry matter.	Per cent. carbohydrate in fresh feces.	Weight of carbohydrate.
	Preliminary Period (5 Days).			
1	43.5	10.19	1.94	0.84
2	43.5	11.60	1.94	0.84
3	60.5	18.37	2.01	1.22
4	73.5	21.87	1.84	1.35
5	136.0	37.66	1.97	2.68
Total	357.0	99.69	..	6.93
Average	71.4	19.94	1.91	1.39
	Water Period (5 Days).			
6	57.5	13.67	1.60	0.92
7	43.5	12.91	1.57	0.68
8	56.5	14.46	1.93	1.09
9	86.5	24.44	1.95	1.68
10	93.5	26.85	2.19	2.06
Total	337.5	92.33	..	6.43
Average per day	67.5	18.47	1.92	1.29
	Final Period (5 Days).			
11	72.0	19.58	1.66	1.20
12	66.5	18.07	1.91	1.27
13	72.5	18.25	1.83	1.33
14	74.5	17.28	1.57	1.17
15	72.5	16.44	0.97	0.70
Total	358.0	89.62	.	5.67
Average per day	71.6	17.92	1.59	1.13

Subject V.—In this case, the daily output of carbohydrates before the water period was 1.44 grams, 1.30 grams were excreted daily during the period of water ingestion, and 1.32 grams daily in the final period (see Table V). Here, again, the actual percentage utilization of the carbohydrate of the diet was the same in each of the experimental periods; the data indicating that 99.51% of the ingested carbohydrate was utilized during the preliminary period, 99.56% during the time of high water ingestion and 99.55% in the final period.

TABLE V.—CARBOHYDRATE EXCRETION—SUBJECT V.

Stool No.	Weight of stool.	Weight of dry matter.	Per cent. carbohydrate in fresh feces.	Weight of carbohydrate.
	Preliminary Period (5 Days).			
1	48.5	10.17	1.01	0.49
2	56.5	13.65	1.54	0.87
3	244.5	47.09	1.10	2.69
4	154.5	27.19	1.13	1.74
5	115.5	22.23	1.24	1.43
Total	619.5	120.33	.	7.22
Average	123.9	24.07	1.17	1.44
	Water Period (5 Days).			
6	56.0	10.65	1.07	0.60
7	75.5	16.90	1.61	1.21
8	44.5	7.05	1.50	0.67
9	120.0	26.75	1.40	1.68
10	171.5	38.60	1.36	2.33
Total	467.5	99.95	.	6.49
Average	93.5	19.99	1.39	1.30
	Final Period (5 Days).			
11	162.5	32.97	1.28	2.08
12	124.5	23.89	1.06	1.32
13	56.5	11.90	1.39	0.79
14	214.0	34.52	1.13	2.42
Total	557.5	103.28	..	6.61
Average per day	111.5	20.66	1.18	1.32

The utilization values for the two subjects for each period of the study are summarized in Table VI.

TABLE VI.—UTILIZATION OF FAT AND CARBOHYDRATE.

	Subject C.		Subject V.	
Period.	Fat. %	Carbohydrate. %	Fat. %	Carbohydrate %
Preliminary	96.14	99.52	96.15	99.51
Water	96.43	99.56	96.00	99.56
Final	96.50	99.62	96.82	99.55

Summary.

Two young men were maintained upon a uniform diet, and the effect of the copious ingestion of distilled water with meals upon the utilization of the ingested fat and carbohydrate determined. The utilization of these nutrients was apparently uninfluenced by the drinking of large volumes of water at meal time.

PHILADELPHIA, PA

[FROM THE LABORATORIES OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND OF JEFFERSON MEDICAL COLLEGE.]

STUDIES ON WATER DRINKING. XVII. THE AMMONIA OUTPUT AS AN INDEX OF THE STIMULATION OF GASTRIC SECRETION FOLLOWING WATER INGESTION.

BY F. WILLS AND P. B. HAWK.

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It is apparent from the literature, so far as we have been able to determine, that Heidenhain[1] was the first authority to advance the view that water stimulated the flow of gastric juice. Somewhat later Sanotskii[2] came to the same conclusion. It remained, however, for Pavlov[3] and his collaborators to place this important physiological-chemical fact upon a firmer experimental foundation. By the use of dogs possessing the Pavlov stomach they showed that the ingestion of 400–500 cc. of water stimulated the flow of gastric juice, and moreover that this stimulation was chemical in character rather than of nervous origin, inasmuch as it was effective following the severing of the vagus nerves. Their experimental data indicate that they were unable, in several instances, to demonstrate any stimulatory power for small volumes of water, *i. e.*, 100–150 cc. They concluded, therefore, that "a prolonged and widely spread contact" with the gastric mucosa was essential for the most efficient stimulation.

Rather more definite data, which are of a wider physiological significance than are those of Pavlov and his collaborators, have been submitted by Foster and Lambert.[4] Dogs provided with Pavlov stomachs were utilized. It was observed when large volumes of water were included in the dietary of the animals that the orifice of the small stomach invariably "appeared raw and inflamed" upon the following day, whereas when the water ingestion of the animals was maintained at a low level, these pronounced indications of irritation were not in evidence. These observations led the authors, in question, to investigate the influence of the water content of the diet upon the secretion of gastric juice. It was found that volumes of water below 200 cc. exerted no appreciable or uniform stimulation. When larger volumes were fed, however, *e. g.*, 40 cc. per kg. body weight, a marked increase in the flow of gastric juice was in evidence. This increase was moreover proportional to the volume of water ingested. The efficiency of water was shown likewise in connection with certain milk feeding tests. In one instance the volume of juice secreted upon feeding 500 cc. of milk, concentrated by evaporation to

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[1] *Pflüger's Arch.*, 19, 148 (1879).

[2] *Arch. sci. biol.*, 1, 588 (1892).

[3] "The Work of the Digestive Glands," translated by Thompson, second edition, p. 112, London (1910).

[4] *Jour. Exp. Med.*, 10, 820 (1908).

250 cc., was only $^4/_5$ as great as that secreted upon the ingestion of 500 cc. of normal milk.

The most significant observation made by Foster and Lambert was to the effect, that the gastric juice secreted in the small stomach under the influence of water ingestion was not only increased in volume, but in its acid concentration as well. For example, when 300 grams of meat was fed a dog the acid value of the juice, at the fourth hour, expressed in terms of 0.1 N NaOH,[1] was 80, whereas when 500 cc. of water were added to an equivalent quantity of meat the acid value rose to 138. This high acid value was obtained notwithstanding the fact that the actual volume of juice was much increased under the influence of the water. It appears, therefore, that "when the secretion is abundant the acidity is much higher than when the secretion is scanty." The same phenomenon has been reported by Ketscher,[2] one of Pavlov's associates. This variation in acidity was believed to be due to the fact that the rapidly secreted juice had less opportunity to come into contact with the alkaline gastric mucosa. On the basis of Ketscher's tests, Pavlov concluded that the juice, if prevented from coming into contact with the mucosa, would possess a similar acid concentration under all conditions, *i. e.*, whether secreted slowly or rapidly. Foster and Lambert call attention to the fact that if this claim of a constant acid concentration, as stated by Pavlov, be true, then "the gastric secretion would form an exception to present ideas of glandular activity." On the basis of carefully performed tests, Foster and Lambert concluded that there was "a variation in percentage content of hydrochloric acid in gastric juice at different times during digestion."

That water stimulates the flow of gastric juice has again been demonstrated very recently by Sawitsch and Zeliony,[3] who showed that the introduction of water in the pyloric portion of the stomach caused a flow of gastric juice in the fundus.

Description.

The subjects of the experiments herewith reported were two men "E" and "W," who had been used by one of us as subjects of other experiments.[4] The particular data under consideration were obtained in connection with certain experiments reported by Mattill and Hawk.[5] Reference may be made to these articles for a full description of experimental conditions surrounding the investigation.

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[1] The number of cubic centimeters required to neutralize 100 cc. of gastric juice.

[2] Pavlov, *Loc. cit.*

[3] *Pflüger's Arch.*, 150, 123 (1913).

[4] Hawk, *Arch. Int. Med.*, 8, 382 (1911). Hattrem and Hawk, *Ibid.*, 7, 610 (1911). Howe, Mattill and Hawk, THIS JOURNAL, 33, 568 (1911). Mattill and Hawk, *Ibid.*, 33, 1978 (1911); 33, 1999 (1911); 33, 2019 (1911).

[5] Mattill and Hawk, THIS JOURNAL, 33, 1978, 1999, 2019 (1911).

Discussion.

In the course of one of the earlier of our studies on water drinking[1] it was observed that the ingestion of an increased volume of water at meal-time caused *an augmentation in the output of urinary ammonia.* In the light of the findings of Pavlov and of Foster and Lambert, already cited, and of Walter[2] and others on *acid ingestion,* it was believed that these high ammonia values might logically be interpreted as indicating that the water had stimulated the flow of gastric juice. The more efficient utilization of the protein constituents of the diet which accompanied these findings furnished further substantiation for the above interpretation.

Bearing the above points in mind the ammonia data obtained in the present investigation were given careful consideration in order to determine whether any further confirmation could be obtained for the hypothesis already advanced. It was clearly apparent from a cursory examination of the data that the output of urinary ammonia had been *markedly increased* under the influence of an increased water ingestion. This fact, when taken into consideration in connection with the further fact that there was an accompanying better digestion and utilization of the ingested protein,[3] was also considered as confirmatory evidence in favor of the hypothesis.

It so happened that "E" and "W" were each subjected to the influence of varying volumes of water, so-called *moderate* and *copious* water drinking, the accompanying ammonia determinations being made in each instance. The completed data indicated clearly that the increase in the ammonia excretion was more pronounced in the case of the larger water ingestion. When this question of relationship was considered more in detail it was found that *during the periods of increased water ingestion there was, in each instance, an increase in the ammonia excretion which was directly proportional to the extra volume of water ingested.* We arrived at this conclusion by means of the calculations embraced in a following paragraph:

TABLE I.—DAILY AMMONIA EXCRETION AS INFLUENCED BY WATER DRINKING WITH MEALS.

	Subject W.		Subject E.	
Period.	Expt. I. Copious water ingestion. 3000 cc. Gram.	Expt. II. Moderate water ingestion. 1500 cc. Gram.	Expt. III. Copious water ingestion. 4000 cc. Gram.	Exp. IV. Moderate water ingestion. 1500 cc. Gram.
Preliminary..........	0.214	0.217	0.212	0.166
Water..............	0.426	0.338	0.367	0.227
Final..............	0.286	0.226	0.246	0.180
		Increase due to water.		
	0.212	0.121	0.155	0.061

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[1] Fowler and Hawk, *J. Exp. Med.,* **12,** 388 (1910).

[2] *Arch. exp. Path.,* **7,** 148 (1877).

[3] Mattill and Hawk, THIS JOURNAL, **33,** 1999 (1911).

If we examine Table I, it will be noted, from a consideration of the data there summarized,[1] that an ingestion of 3000 cc. of water at meal-time above that customarily ingested caused an average daily increase of 0.212 gram in the ammonia excretion of subject W, whereas an ingestion of 1500 cc. by this same subject caused an increase of only 0.121 gram in the ammonia output. In like manner, it will be observed that an addition of 4000 cc. to the water ingestion of subject E caused an increase of 0.155 gram in the ammonia excretion, whereas when the volume of ingested water was 1500 cc. the ammonia output was augmented by only 0.061 gram.

Let us consider the data more in detail. We will first consider the data from the experiments on subject W. To facilitate the following of the relationship mentioned the data will be presented in logical mathematical sequence.

MODERATE WATER DRINKING (Subject W).

Volume of milk ingested per day	1200 cc.
Percentage of water in milk	87%
Volume of water in 1200 cc. milk	1044 cc.
Volume of water ingested per day *with meals* in preliminary period	300 cc.
Total volume of water ingested per day *with meals* in preliminary period, *i. e.*, water plus water content of milk	1344 cc.
Volume of increased water ingestion taken daily *with meals* during *water period*	1500 cc.
Percentage increase in water *ingested at meal time*	112%

COPIOUS WATER DRINKING (Subject W).

Volume of milk ingested per day	1350 cc.
Volume of water in 1350 cc. milk	1175 cc.
Volume of water ingested per day *with meals* in preliminary period	300 cc.
Total volume of water ingested per day *with meals* in preliminary period, *i. e.*, water plus water content of milk	1475 cc.
Volume of increased water ingestion taken daily *with meals* during water period	3000 cc.
Percentage increase in water *ingested at meal time*	203%
Ratio between the percentage increase in the daily *ingestion of water with meals* during the water periods of the experiments on moderate (112%) and copious (203%) water drinking	1 : 1.81
Ratio between the increased *output of ammonia* under moderate (0.121 gram) and copious (0.212 gram) water drinking with meals	1 : 1.75
Ratio between water ingestion and ammonia excretion	1 81 : 1 75
The similar ratio for Subject E is	2 66 : 2 54

We see from these ratios that there was practically a *quantitative* relationship between the water ingestion and the ammonia excretion. In other words, *the increase in the ammonia excretion was directly proportional*

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[1] The ammonia values for the individual days will be presented in a later paper in connection with other data on nitrogen distribution.

to the increase in the volume of water ingested. We have interpreted the above findings as indicating that the water ingestion stimulated the flow of gastric juice thus causing the production of a greater quantity of hydrochloric acid and that this increased acid production was the forerunner of an increased ammonia output (see later discussion). The uniform relationship between the water ingestion and the ammonia output might perhaps be considered as indicating that there was an attempt on the part of the gastric cells to maintain a *uniform acid concentration.*

TABLE II.—WATER AND AMMONIA RATIOS.

Subject W.		Subject E.	
Expt. I. $\frac{\text{Copious } H_2O}{\text{Moderate } H_2O}$	Expt. II $\frac{NH_3 \text{ inc. (cop.)}}{NH_3 \text{ inc. (mod.)}}$.	Expt. III. $\frac{\text{Copious } H_2O}{\text{Moderate } H_2O}$.	Expt. IV. $\frac{NH_3 \text{ inc. (cop.)}}{NH_3 \text{ inc. (mod.)}}$.
1 : 1.81	1 : 1.75	1 : 2.66	1 : 2.54
Increased NH_3 per 100 cc. H_2O (grams).			
3000 cc. H_2O.	1500 cc. H_2O	4000 cc. H_2O.	1500 cc. H_2O.
0.0071	0.0081	0.0039	0 0040

When we compute the amount of ammonia excreted for every increase of 100 cc. in the water ingestion we find a significant relationship. The values thus secured are shown in the lower portion of the above table. In the tests made upon subject W it will be seen that each 100 cc. of the three liters of water added to the water ingestion during the interval of copious water drinking caused an increase of 0.0071 gram in the ammonia output, whereas when the water ingestion was increased only 1500 cc. each 100 cc. augmented the ammonia excretion 0.0081 gram. A similar relationship held for subject E. In other words, when we calculate the increased ammonia excretion upon the basis of a 100 cc. increase in the water ingestion, we find that the excretion was a trifle higher during moderate water drinking than during the period of copious water ingestion. These findings might be interpreted as indicating that after a certain limit had been reached in the water ingestion, each succeeding 100 cc. of water was less efficient as a stimulating factor than were the 100 cc. portions ingested before the limit above mentioned had been reached.

When we compare the data from the two subjects we obtain interesting information regarding the reaction of different individuals to similar stimuli. In the moderate water drinking tests, for example, Subjects E and W each increased their water ingestion by 1500 cc. If the ammonia values be consulted it will be noted that the ammonia output was increased 0.121 gram in the case of W and 0.061 gram in the case of E. In other words, identical stimuli proved twice as efficient in the organism of W as in that of E. A similar type of relationship is in evidence in connection with the tests on copious water drinking. Here it was demonstrated that 4000 cc. of water in E's organism was only about 73% as efficient as a stimulatory factor as was 3000 cc. in W's organism.[1] It is entirely logical to infer furthermore that the response of the same individual to identical stimuli will not always be the same. For example, it is entirely possible that three liters of water would not, under all conditions, cause sufficient stimulation of the gastric secretion of W to cause an increase of 0.212 gram in the output of ammonia. In other words, we do not wish to be understood as claiming that a variation in the water ingestion of an individual will, of necessity, be accompanied by a quantitative relationship between the associated ammonia excretions.

In order to substantiate our acceptance of the increased ammonia output as an index of a stimulated gastric secretion, permit us to make certain potent citations from the literature. In the first place we would call attention to various investigations upon man and the lower animals which have demonstrated clearly that the feeding of mineral acids and acid salts is followed by an increased excretion of urinary ammonia.

The balance of acids and bases in the animal organism has a very pronounced influence upon the extent of the ammonia output. Experiments have demonstrated conclusively that the acids present in the organism cause an increase in the excretion of ammonia, irrespective of whether such acids are introduced from without or are formed in the processes of intermediary metabolism. These acids have been considered as neutralizing a part of the ammonia and thus withdrawing it from participation in the formation of urea. Walter[2] was the first to demonstrate that acids possessed this influence. This investigator fed hydrochloric acid to dogs and secured an increased output of urinary ammonia. Hallervorden,[3] after ingesting 2.81 grams of hydrochloric acid on each of two days, secured an increase in the ammonia output aggregating 2.035 grams for a five-day interval. Kowalevsky and Salaskin[4] fed 6 grams of hydrochloric acid to a fasting goose and increased the percentage of the total nitrogen excreted as ammonia nitrogen from 14.98% to 33.36%. Certain experiments by Eppinger[5] and Winterberg[6] indicate that an increased ammonia elimination also follows the administration of mineral acids to rabbits. Kettner[7] and Pohl and Münzer,[8] on the other hand, failed to obtain such an increase in the case of herbivora.

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[1] E was receiving 20.4 cc. water per kg. body weight; W was receiving 23.6 cc.

[2] *Arch. exp. Path.*, 7, 148 (1877).

[3] *Ibid.*, 10, 125 (1878).

[4] *Z. physiol. Chem.*, 35, 552 (1902).

[5] *Z. exp. Path.*, 3, 530 (1906).

[6] *Z. physiol. Chem* , 25, 202 (1898).

[7] *Arch. exp. Path.*, 47, 178 (1907).

[8] *C. Physiol.*, 20, 232 (1906).

It has been suggested by Hallervorden[1] and Coranda[2] that man takes an intermediate position between carnivora and herbivora so far as the intensity of the stimulatory power of ingested acid upon the urinary ammonia output is concerned.

That the daily ammonia output may be taken as an index of the course of diabetic acidosis is well recognized. Müller was the first to demonstrate that a pronounced increase in the ammonia excretion followed extensive acidosis.[3] Cases of diabetes mellitus occasionally excrete from 7 to 12 grams of ammonia per day, whereas the normal output is approximately 0.7 gram.[4]

It is, furthermore, a well-known fact in normal nutrition that there is an increase in the urinary ammonia output when a high protein diet is ingested. This is principally due to the excessive quantity of sulfuric acid formed in the oxidation of such a diet. A portion of this ammonia may also arise from increased intestinal putrefaction.

The above citations from normal and pathological metabolism in which there is an increased acid production in the body, and the experiments on man and lower animals in which mineral acids have been ingested, all indicate that such acid production or ingestion is followed by an increased output of ammonia in the urine. Therefore, inasmuch as it has been shown by experiment that water stimulates the flow of gastric juice and that consequently there is an augmented secretion of acid, we feel warranted in advancing the hypothesis that the increased ammonia excretion which accompanies the drinking of water at meal time is brought about through the stimulatory power of the ingested water.

In view of the recent claim of Folin and Denis that the ammonia of the portal circulation has its origin in large part in putrefactive processes taking place in the large intestine, it might be argued that the drinking of water has caused increased putrefaction. From this standpoint, then, the high ammonia values which the urines in our water experiments possess might be considered to be an index of increased intestinal putrefaction. Fortunately, however, the course of intestinal putrefaction, in the experiments in question, was followed by Hattrem and Hawk.[5] They found the output of urinary indican *much decreased* during the period of water drinking. If indican is a true index of intestinal putrefaction we must conclude that the high ammonia values occurred coincidently with a decreased intestinal putrefaction and that the major part, at least, of the ammonia did not have a putrefactive origin.

[1] *Arch. exp. Path.*, 10, 125 (1878).

[2] *Ibid.*, 12, 76 (1880).

[3] Lusk, *J. Am. Med. Assoc.*, Dec. 17, 1910.

[4] Magnus-Levy, *v. Noorden's Handb. d. Path. d. Stoffwechsel*, 1, p. 115.

[5] Hattrem and Hawk, *Arch. Int. Med.*, 7, 610 (1911).

Conclusions.

The ingestion of water at meal time by two men was accompanied by an increase in the excretion of ammonia which was *directly proportional to the extra volume of water ingested.* Inasmuch as certain experiments have demonstrated that water *stimulates the flow of an acid gastric juice* and as certain other experiments have demonstrated that the formation of acid in the body or the introduction of acid from without produces *an increase in the urinary ammonia excretion,* we feel justified in assuming that the increase in the ammonia excretion observed in our experiments was *due directly to the stimulation of gastric secretion by the ingested water.*

The uniform relationship between the water ingestion and the ammonia output might perhaps be considered as indicating that there was an attempt on the part of the gastric cells to maintain *a uniform acid concentration.*

If we calculate the increased ammonia excretion, on the basis of a 100 cc. increase in the water ingestion, we find that the excretion was a trifle higher during moderate water drinking than during copious water drinking. This would indicate that after a certain limit had been reached in water ingestion each succeeding 100 cc. of water was less efficient as a stimulating factor than were the 100 cc. portions ingested before the limit above mentioned had been reached.

That different organisms may respond differently to identical stimuli was indicated by the fact that the increase in the ammonia output of one subject was 100% greater than that of the other subject, notwithstanding the fact that the increase in the water ingestion was the same in each instance.

That the increase in the ammonia excretion *did not arise from intestinal putrefaction* was indicated by the finding of *lowered indican values* during the period of high water ingestion.

PHILADELPHIA, PA

[CONTRIBUTION FROM STEVENS INSTITUTE OF TECHNOLOGY]

A REVIEW OF THE PIONEER WORK ON THE SYNTHESIS OF RUBBER.[1]

BY FRANCIS J. POND.

Received November 7, 1913

At a meeting of the chemical society of Heidelberg on May 19, 1906, Prof. E. Knoevenagel[2] presented a paper in which he described two new hydrocarbons, C_6H_{10}, belonging to the $\Delta^{1,3}$-butadiene series. One of these hydrocarbons was found to yield a dimolecular polymeride, $C_{12}H_{20}$, and it was suggested that its formation was possibly similar to the formation of dipentene, $C_{10}H_{16}$, by the polymerization of isoprene, C_5H_8.

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[1] Read before the New York Section of The American Chemical Society, Oct. 10, 1913.

[2] *Z. angew. Chem.*, [2] 19, 1330.

It was also stated that the investigation of these two hydrocarbons would be continued, especially to determine whether, by other methods of polymerization, it would be possible to prove a relationship between these compounds and the rubber group.

In the discussion following the reading of this paper, Prof. A. Klages[1] stated that he had been occupied for a long time with the study of the homologues and analogues of isoprene, and other hydrocarbons of the butadiene series. He had found that the members of this group almost without exception possess the property of yielding dimolecular compounds when treated with sulfuric acid.

Professor Klages further stated that he had tested a large number of these hydrocarbons, especially with a view to the possibility of converting them into rubber-like substances. Notwithstanding the fact that he had made many experiments with these hydrocarbons, including isoprene, he had never been able to isolate a product having the well-known elasticity and nerve of true rubber, not even from isoprene. Further, the hydrocarbons formed from sorbinic acid, according to Doebner, possess a structure showing the greatest analogy with 1,5-dimethylcyclooctadiene, a substance which Harries describes as the parent hydrocarbon of the rubber series; even these hydrocarbons have never been converted into rubber-like products.

Accordingly, Prof. Klages said it was his opinion that the close relationship of isoprene to rubber, which had up to that time been ascribed to this hydrocarbon, had no justification; and the statements that isoprene can be converted into rubber-like substances do not correspond with the facts, and it was therefore time to strike such statements out of the literature.

On March 12, 1910, in Vienna, Prof. C. Harries[2] delivered a lecture on the chemistry of rubber. During this lecture he stated that until most recent times all experiments on the synthesis of rubber have failed, and Klages has declared that, according to his experiences, it is absolutely impossible to convert isoprene into rubber. Continuing, Prof. Harries stated the following:

"During the past seven years or so, at different times and with many different co-workers, I have repeated the work outlined by Tilden, and have never been able to confirm his results. Also I am advised that the same thing has been done by others with the same negative results. I exhibit here a preparation consisting of isoprene which was saturated with hydrochloric acid gas three months ago; aside from some darkening in color, it is absolutely unaltered. If isoprene is treated with organic acids and is then allowed to stand, there is no appreciable change to be observed even after many months; formic acid alone causes the isoprene to resinify quickly. Therefore, Tilden must have quite accidently hit upon certain conditions in his experiments, which caused the polymerization of isoprene. But the most important point relative to Tilden's work is that he never proved that he actually had rubber in his hands, for, as I will illustrate later, isoprene may be converted into all sorts of products which might be described as rubber-like, although they really have very little to do with rubber. Thus, after long standing in the presence of air, isoprene certainly becomes viscous, but this is not caused by polymerization; it forms a peroxide which is very explosive when heated. Therefore, in view of my own experiences, I was for a long time of the same opinion as Klages.

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[1] *Z. angew. Chem.*, [2] 19, 1330; *Gummi-Ztg.*, 23 (Sept. 21, 1906), 1277

[2] *Gummi-Ztg.*, 24 (March 18, 1910), 851; see also *Chem. Ztg.*, 34, 315.

"My interest in this particular direction was renewed last summer when, upon the recommendation of Geh. Rat. Hempel of Dresden, I was asked by a large English firm if I was in the position to determine for them whether a certain sample of a rubber-like product was real rubber. This sample was alleged to have been prepared by a process patented in England by a Dr. Heinemann, and the process was said to consist in passing acetylene, ethylene and methyl chloride simultaneously through a red-hot tube. This was alleged to first form isoprene, which was then at once polymerized to rubber. I at once determined that the sample in question really was a true rubber, but its outward appearance was devilishly (verteufelt) similar to that of old para-rubber. I advised the firm that the sample in question was actually rubber, but I especially emphasized the fact that before they should take any further steps in the matter, they should be absolutely convinced that the sample sent to me had actually been prepared by Dr. Heinemann's process. For a long time I have taken special pains to repeat this process, and I know that others also have tried to reproduce it; but neither I nor the other chemists have been able to confirm in the slightest particular the statements given in the English patent. If isoprene and rubber can actually be obtained by this process, then there are such special conditions necessary that they should have been clearly stated in the patent, and to anyone who rediscovered these special conditions, I, as a competent judge, would give the right to patent them as new in Germany. As a matter of fact, however, I do not believe that the process works at all; according to our practical experiences it is extremely improbable.

"However, by means of these experiments I came back to isoprene and directed my work to new syntheses of isoprene and to its polymerization. On the first of November, 1909, Geh. Rat. Duisberg of the Elberfeld Farbenfabriken sent me some samples of artificial rubber, which were alleged to have been prepared from isoprene by a process invented by Dr. Fritz Hofmann; the details of the process, however, were not given to me. I was asked to determine whether these samples contained true rubber. I was able to determine that these samples were true rubbers in every particular, and, therefore, artificial rubber was prepared from this side for the first time."

On June 17, 1912, Prof. W. H. Perkin, Jr., read a paper[1] on "The Production and Polymerization of Butadiene, Isoprene, and their Homologues," before the London Section of the Society of Chemical Industry. I quote the following paragraphs from Prof. Perkin's paper:

"As regards the history of this synthesis, it seems to me desirable, in view of statements which have been made abroad, to review the work of earlier investigators, and particularly that of W. A. Tilden in England, and G. Bouchardat in France, in order that I may emphasize the fact, as I particularly wish to do, that much of the credit of the pioneer work in this subject belongs to this country and to France.

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[1] *J. Soc. Chem. Ind.*, 31, 616.

"It is surprising that Prof. C. Harries should doubt whether Tilden really had synthetic rubber in his hands in 1882 and 1884, and should advance the view that certain samples produced in 1909 by Bayer & Co., of Elberfeld, were the first true samples of synthetic rubber. This criticism is quite beside the mark, and the specimens of crude synthetic rubber which Tilden undoubtedly prepared were made many years before Bayer & Co. produced rubber by their process."

"It is of very great interest to notice that an Englishman, Greville Williams, who, in 1860, was the first to isolate isoprene from the products of the destructive distillation of rubber in a fairly pure state, was also the first to observe the transformation of this hydrocarbon into a rubber-like body." "It is true that this substance, which Greville Williams regarded as an oxide, was not at his disposal in sufficient quantity, or purity for him to definitely identify it with rubber (which it undoubtedly contained), but it is clear from his remarks that he considered that both caoutchouc and gutta-percha are polymers of isoprene."

"In 1875 G. Bouchardat showed that isoprene is converted by heating in a sealed tube into a mixture of polymers, including the indefinite substance named colophene, which there can be no doubt contained a considerable proportion of rubber."

"It is a remarkable tribute to Tilden's intuition that he should not only at this early date (1882) have foreseen the successful production of synthetic rubber, but he should also at the same time have suggested the correct formula for isoprene."

"In 1892 Tilden showed for the first time that synthetic rubber is capable of vulcanization and therefore sufficiently resembles natural rubber to be used commercially, if some means could be discovered for producing it in quantity."

"Harries and Klages were tempted, as has already been stated, to throw doubt on the validity of Bouchardat's and Tilden's polymerisation results; this, in spite of the confirmatory work of many other investigators on isoprene and its homologues to which I have already alluded. But no one who is really conversant with the literature of the subject, or who has had the opportunity of inspecting the preparations made by Tilden, can, for a moment, doubt that Tilden had polymerized isoprene to rubber as far back at least as 1884. And similarly there can be no doubt that Bouchardat had synthetic rubber in his hands as far back as 1875."

"I wish to emphasize the fact, which on more than one occasion has been overlooked, that much of the pioneer work in connection with the discovery, production, and with the polymerization of isoprene was carried out in this country."

On September 9, 1912, Geh. Rat. Dr. Carl Duisberg of Elberfeld, Germany delivered his extremely interesting and brilliant address before the Eighth International Congress of Applied Chemistry, in New York City. The subject of this general lecture was "The Latest Achievements and Problems of the Chemical Industry,"[1] and reprints of this lecture were distributed at the time of the address. As I recall it, the address followed almost exactly word for word the text given in the reprint, and I will quote some paragraphs as given in this reprint:

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[1] "Transactions and Organization," *Eighth International Congress of Applied Chemistry*, Vol. 28, pages 50 and 86.

Page 29 of reprint. "I will refer to one of the greatest successes and yet one of the most difficult problems of the chemical industry, *viz.*, the production of synthetic rubber. I am proud of the fact that its production was successfully accomplished in the works which are under my management, and that I was able to follow every stage of this important discovery. Perhaps you would be interested to hear how the whole thing happened, especially as much that is untrue and misleading has appeared in the press during the last few weeks."

Page 30. "By breaking up the very complex molecule which rubber doubtless possesses, by pyrogenetic processes, *i. e.*, by dry distillation, a veritable maze of all kinds of gases, oils and resins was obtained, as well as a colorless fluid resembling benzine, to which the investigators gave the name 'Isoprene.' It was the French scientist Bouchardat who first expressed the belief that this isoprene, which is obtained in very small quantities and in an impure form by the dry distillation of caoutchouc, might be closely and intimately related to caoutchouc itself. This important question was then eagerly discussed for several decades by the scientists of all countries and opinions were sharply divided. As far back as the eighties, the Englishman Tilden claimed to have prepared artificial rubber from isoprene by treatment with hydrochloric acid. But neither Tilden nor his assistants, though they worked strenuously for years, succeeded in repeating the experiments. Moreover, numerous other investigators were unable to confirm the results. Dr. Fritz Hofmann of the Farbenfabriken vorm. Fried. Bayer & Co. is to be regarded as the real discoverer of synthetic rubber, for, by the application of heat, he succeeded, in August, 1909, in polymerizing the isoprene molecules into the complex rubber molecule. Somewhat later Harries discovered independently another method of arriving at the same result. Everyone is now in a position to repeat this exceedingly simple experiment himself, but in order to confirm Hofmann's results, it is necessary to employ *pure* isoprene."

I find that this address was changed in certain points before its final publication in Volume 28, of the Transactions of the Eighth International Congress of Applied Chemistry. The changes occur in the above quoted paragraph commencing with the statement, "Moreover, numerous other investigators," etc. Since these changes are important, I will quote this particular part as printed on pages 113 and 114 of Volume 28:

"Moreover, numerous other investigators, among them our chemists, were unable to confirm the results. In 1894 Tilden found, however, that that isoprene which he had prepared about ten years before, on standing, had partially polymerized into rubber. In this way Tilden in fact was the first discoverer of synthetic rubber. But this method which time has not yet permitted to repeat, is obviously not a commercial one. Dr. Fritz Hofmann of the Farbenfabriken vorm. Fried. Bayer & Co. is to be regarded as the real inventor of synthetic rubber, for, by the application of heat, he succeeded as the first in August, 1909, in polymerizing the isoprene molecules completely into the complex rubber molecule on a technical scale."

Continuing his address, Geh. Rat. Duisberg said: "Isoprene belongs to the butadienes. It was therefore to be assumed at the start that β-methylbutadiene would not hold a peculiar and isolated position among the butadienes in general. It was argued that other members of this interesting group of hydrocarbons would yield analogous and homologous rubbers on being heated." "Exact proof of the existence of the class of isomeric and homologous caoutchouc was also first presented by Elberfeld."

In a paper[1] by Dr. F. M. Perkin, read before the Royal Society of Arts on December 11, 1912, the author referred to the pioneer work on synthetic rubber in the following paragraphs:

"In all probability, Greville Williams (in 1860) had actually produced synthetic rubber."

"The first real proof of the polymerisation of isoprene to form rubber was by Sir William Tilden in 1882."

"It having been shown by Tilden, and confirmed by other workers, that isoprene on polymerisation formed rubber, the chief efforts of investigators in the first place were directed to obtain a satisfactory and cheap method for the preparation of isoprene."

"About 1899 or 1900, Kondakow showed that other members of the isoprene or divinyl series could be polymerised into rubber-like bodies, either by exposure to light, or on keeping, or by means of chemical agents."

In a monograph[2] on 'The Synthesis of Rubber' by Dr. Rudolf Ditmar, published in 1912, the author says:

"The synthesis of rubber was made possible only by the work of Prof. C. Harries explaining the constitution of the rubber molecule. It is true that the synthesis of rubber from isoprene was accomplished long before Harries' work on the constitution of rubber, but without the scientific back-ground furnished by Harries, this synthesis by Bouchardat would be in a sorrowful position." "Owing to Harries' work alone, we can now say 'rubber must be prepared from isoprene;' and since the publication of Harries' work, the syntheses of rubber have proceeded along scientific lines."

"By heating isoprene with dilute acids, Bouchardat, in 1879, obtained an elastic polymeride, which, after boiling with water, possessed the properties of rubber. This first synthesis of rubber by Bouchardat was confirmed by W. A. Tilden and O. Wallach. However, the statements of these investigators agree that it was impossible to determine the experimental conditions necessary for the synthetical preparation of rubber."

"The first useful technical method for the synthesis of rubber was announced, in a patent by the Farbenfabriken vorm. Friedrich Bayer & Co. of Elberfeld under date of September 11, 1909."

In a paper dated November 12, 1912, and published in the *Annalen*[3] on January 30, 1913, Prof. Harries refutes the claim to priority in the field of synthetic rubber advanced by Perkin, Jr. and others. There is much in this paper which I shall wish to quote later on, when considering details, but there is one portion which I think should be given here.

Prof. Harries says: "It is only about two years since my last paper[4] on synthetic rubber was published, and this paper has produced a remarkable literary activity. For 10 years I believed I was working alone in the field of rubber chemistry, when all at once I discovered that chemists everywhere had been working on the same problems even before my work. However, the publication of these various papers first began to appear after my lecture in Vienna in 1910, in which I mentioned certain eventually successful practical results. But this result of my lecture would have been very welcome, had there not appeared less agreeable features, which probably never before appeared to such an extent in any other field of chemistry; I refer to the introduction of nationalistic motives into scientific research, and to the broadcast discussion of questions of priority in scientific matters in the daily press, or in certain journals which usually are not selected for such discussions.

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[1] "Natural and Synthetic Rubber," *J. Roy. Soc. Arts*, 61, 92, 93.

[2] "Die Synthese der Kautschuks," von Dr. Rudolf Ditmar, pp. 3, 24, 25.

[3] *Ann.*, 395, 211

[4] *Ibid*, 383, 159.

"What am I to say, when one may see to-day in any newspaper an elaborate account of how Perkin, Jr. has stated in a lecture that English chemists discovered sodium-synthetic rubber six months before I did? I certainly cannot enter into a discussion of priority regarding a scientific question in the daily press!"

"If Russian and English chemists to-day endeavor to especially emphasize the priority of the discoveries in the field of rubber chemistry as strictly Russian or English, then it appears to me a regrettable departure from the customs of the Masters of previous generations, who regarded science as international."

"On July 15, 1912, W. H. Perkin, Jr. delivered a lecture before the London Section of the Society of Chemical Industry, the purport of which in many of its relations challenges contradiction. The purpose of this address is quite apparent, namely, the presentation of the discoveries in the field of rubber and gutta-percha chemistry as purely English accomplishments."

"Really, one can only shake his head as Perkin now seeks to interpret the old, meager statements of Williams relating to the auto-oxidation products of isoprene so that it will appear that Williams really had synthetic rubber in his hands."

In view of these conflicting statements by Klages, Harries, Perkin, Jr., Duisberg, and others, regarding the pioneer work on this subject, it has seemed to me desirable to review, in considerable detail the published work of the earlier investigators. In doing this, I shall quote the exact statements given in the literature, and shall try to quote impartially and in sufficient detail so that each one may arrive at his own conclusion as to the amount of credit due to each of the earlier workers.

Possibly the first important paper on this subject is "On Isoprene and Caoutchine" by the Englishman, C. Greville Williams,[1] published in 1860. In this paper Williams describes certain experiments on the dry distillation of caoutchouc, in which he obtained traces of volatile bases, and two chief distillates, the one boiling between 37° and 44°, the main portion of which distilled between 37° and 38°, and the other boiling between 170° and 180°. The liquid boiling at 37° to 38° was named *isoprene*, while that boiling between 170° and 180° was termed "caoutchine."

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[1] *Phil. Trans.*, 1860, 245; *Proceedings of the Royal Society*, 10, 516.

Under the heading, "Action of Atmospheric Oxygen on Isoprene," Williams states the following:

"If isoprene be left in a partly filled bottle for some months, it gradually loses its fluidity, and at last even becomes quite viscid; at the same time it is found to have acquired powerful bleaching properties. It is, in fact, ozonized."

"On submitting ozonized isoprene to distillation, if the temperature be kept as low as is compatible with the volatilisation of the unaltered portion of the oil, a colorless limpid fluid distils over, having the composition and boiling point of pure isoprene. As the operation proceeds the fluid thickens, causing the temperature to rise somewhat suddenly. The ozone at this point instantly begins to act with energy, a cloudy vapour rises, accompanied by an intensely sharp odour, and the contents of the retort instantly solidify to a pure white, spongy, elastic mass, having, when successfully prepared, but slight tendency to adhere to the fingers. When pure, it is opaque; but if allowed to become exposed to the air, especially when warm, it becomes transparent, first on the edges, and subsequently throughout the whole mass. When burnt, it exhales the peculiar odour hitherto considered characteristic of caoutchouc itself. It is not easy to prepare or to preserve this substance of definite composition. If the heat be allowed to rise too rapidly during its formation, it becomes decomposed; and if not heated sufficiently, a portion of the original hydrocarbon obstinately adheres. However prepared, its composition is that of isoprene plus oxygen. If sufficient care be taken, the oxidation is perfectly definite. A specimen prepared with every precaution, and immediately analyzed gave 78.8% of carbon, 10.7% of hydrogen, and 10.5% of oxygen."

"The above-described substance is, it is believed, unique in its characters, whether we regard its composition as the directly formed oxide of a hydrocarbon or the mode of its production by the influence of ozone."

That Williams regarded caoutchouc as in some way related to isoprene and caoutchine (later termed di-isoprene and dipentene), is shown by his statement "On the Composition of Caoutchouc;" he says: "I am anxious to call attention to the fact that the atomic constitution of caoutchouc appears to bear some simple relation to the hydrocarbons resulting from its decomposition by heat. The composition of caoutchouc coincides with that of isoprene and caoutchine, as found by analysis, to a degree which is remarkable when we consider that caoutchouc, in addition to being non-crystalline, is scarcely capable of purification by chemical means."

A review of this paper in the "Proceedings of the Royal Society of London" for the year 1860 states that Williams "considers the action of heat on caoutchouc to be merely the disruption of a polymeric body into substances having a simple relation to the parent hydrocarbon."

Prof. Perkin, Jr., says that this pure white, spongy, elastic mass, described by Williams as an *oxide of isoprene* and not as rubber, "*undoubtedly contained rubber,*" and Perkin, Jr. evidently seeks confirmation of Williams' work in a patent taken out by A. Heinemann of London in 1910. This patent[1] is on a "Method for the Preparation of Rubber from Isoprene," and it contains the following statements:

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[1] English Patent, No 14041, 1910; Deutsche Patentanmeldung, H54443, Kl. 39 b, June 6, 1911

"This discovery consists in a method for the preparation of rubber by the action of ordinary or nascent oxygen, or ozone, on isoprene. A special characteristic of this discovery consists in the fact that isoprene is first treated with oxygen or ozone, and then heated. On heating, the isoprene first thickens, and then is changed into a substance, which possesses the properties of natural rubber."

Perkin, Jr., says: "this seems to be almost exactly what Greville Williams had described fifty years before."

True; but, in my opinion, this is not sufficient reason for Perkin's assumption that Williams' product "undoubtedly contained rubber." I know of no paper by Perkin, Jr. in which he even attempts to prove that the method described in Williams' paper and in Heinemann's patent actually does give "a substance which possesses the properties of natural rubber." It is hardly safe to base one's conclusions in such a matter on the unverified statement, or patent of another person.

Furthermore, we shall later see where Perkin's use of another Heinemann patent has apparently led Perkin, Jr. into an error, with the result that an injustice was, I think unintentionally, committed against the chemists of Bayer & Co.

In his second paper[1] on the synthetic rubbers, published on January 30, 1913, Prof. Harries refers to Williams' paper and Perkin's comments on it as follows:

"I have previously pointed out that when isoprene is allowed to stand for some time in contact with air in closed bottles, it certainly becomes viscous; however, this treatment does not form rubber, but rather a highly explosive peroxide. If the latter be so heated as to cause an explosion, then it is quite true that an odor similar to that of burning rubber is observed; but the resulting residue does not contain rubber, as Perkin assumes it does. Heinemann's English patent, which Perkin cites to strengthen his claims, does not persuade me to change my views, because it is impossible to regard this man's patent seriously after he states that rubber is produced by heating the reaction-product resulting from the ozonisation of isoprene."

Personally, therefore, I believe it should be especially emphasized that Williams did not say that he prepared rubber, and he certainly gave no proof that his product was rubber, and there has been no subsequent work published to prove that Williams' product was true rubber. To say that his product "*undoubtedly contained rubber,*" is at the present time speculation, and we have no right to call him the *discoverer of synthetic rubber.*

The next important work on the synthesis of rubber to be noted is that by the French chemist, G. Bouchardat, published on June 14, 1875, and December 29, 1879. Since this work has caused considerable debate, I think we should first carefully consider Bouchardat's own words. In his first paper,[2] published in 1875, "On the Synthesis of a Terpilene," Bouchardat says:

"I subjected isoprene, placed in sealed tubes, to a temperature of 280° to 290° for six hours, and excluded the least traces of air in the tubes by means of an atmosphere of carbon dioxide gas.

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[1] *Ann.*, **395**, 217.

[2] *Bull. soc. chim.*, **24**, 108; *Compt. rend.*, **80**, 1446.

"No gas was formed during this action. The product which resulted by the action of heat is entirely changed in its appearance; it is less fluid, viscous; its specific gravity is increased; it no longer boils at a constant temperature of 38°.

"On distillation the product is separated into three chief products, *viz.*, first, a certain proportion of unaltered, original hydrocarbon; second, a hydrocarbon volatile at 170° to 185°; third, products of condensation with a higher boiling point; I have studied chiefly the product volatile at 170° to 185°. The greater part of this distils at 176° to 181°."

"To sum up, isoprene, a hydrocarbon containing only 10 equivalents of carbon, gives, when condensed or polymerized by the action of heat alone, a hydrocarbon containing double the number of carbon atoms, and whose derivatives are identical with those of *terpilene*."

Referring to this paper, Prof. Perkin, Jr. says:

"In 1875, G. Bouchardat showed that isoprene is converted by heating in a sealed tube into a mixture of polymers of isoprene, *viz.*, dipentene, $C_{10}H_{16}$, $C_{15}H_{24}$, etc., including the indefinite substance named colophene, *which there can be no doubt contained a considerable proportion of rubber.*" "*There can be no doubt that Bouchardat had synthetic rubber in his hands as far back as 1875.*"

In my opinion, there is no justification in Bouchardat's words for such a statement. He most certainly does not mention that his higher boiling product (colophene) contained a *trace of rubber*, not to mention "*a considerable proportion.*"

In the light of Bayer & Co.'s patents of 1909, describing the formation of synthetic rubber by heating synthetic isoprene in sealed vessels at 100° to 200°, it is easy to imagine that Bouchardat might have obtained rubber in 1875 if he had used isoprene of equal purity, and had observed the same conditions of temperatures, etc., which these investigators did some 34 years later. But after reading Bouchardat's paper, there seems to me no reason for believing that he had synthetic rubber in his hands in 1875.

Bouchardat's second paper,[1] published in 1879, is on "The Action of the Halogen Acids on Isoprene, and *The Reproduction of Rubber.*" I quote from this paper the following:

"When dry hydrochloric acid gas is passed slowly through isoprene cooled to 0°, it is partially and slowly absorbed, and yields a mobile liquid, having a brown color. When the product is distilled, it yields some unchanged hydrocarbon, and isoprene mono-hydrochloride, boiling at 86° to 91°.

"Under the conditions, *viz.*, three hours of action, the formation of an appreciable quantity of a substance having a higher boiling point is not observed."

"Hydrochloric acid, in a solution saturated at 0°, acts differently upon isoprene than does the dry gas. One part of isoprene was treated in the cold in a sealed vessel with 12 to 15 parts of the acid. A vigorous reaction, indicated by a notable rise in the temperature of the mixture, took place immediately upon agitation; the whole was left at the room temperature for 15 to 20 days, agitating only from time to time. The contents of the tube were then added to water and submitted to distillation as long as oily drops were obtained. There remained, with the excess of acid water, a solid residue in notable proportions.

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[1] *Compt. rend.*, 89, 1117, 1118, 1119.

"The volatile products resulting from the distillation included no unchanged hydrocarbon; it yielded one-fifth of its volume of a substance boiling at 85° to 91°, the remainder boiling at 145° to 153°. There was no substance boiling at a higher temperature.

"The first substance possessed the composition and properties of isoprene mono-hydrochloride, $C_{10}H_8HCl$.

"The second product, boiling at 145° to 153°, possessed the composition of a dihydrochloride of isoprene, $C_{10}H_8.2HCl$.

"The last product of the action of the acid upon isoprene is non-volatile (fixed). After this substance is treated for a long time with boiling water in order to free it from chlorine-containing substances, which accompany it, and which it obstinately retains, it has the percentage composition of isoprene. It contains little more than one part per hundred of chlorine, which may be due to the fact that it retains some of the volatile chlorinated compounds, or it may be due to the fact that the compound itself combines partially with hydrochloric gas ($C = 87.1$; $H = 11.7$; $Cl = 1.7$). Furthermore, it possesses the elasticity and other characteristics of rubber itself. It is insoluble in alcohol; it swells up in ether, also in carbon disulfide in which it dissolves in the manner of natural rubber. When the product is submitted to dry distillation, it forms the same volatile hydrocarbons as rubber; I have isolated from these distillation products a certain quantity of a hydrocarbon, $C_{20}H_{16}$, which, when treated with hydrochloric acid, gave me the dihydrochloride, $C_{20}H_{16}.2HCl$, melting at +46°, the same as the dihydrochloride from caoutchouc. This fact constitutes a new method for the synthesis of terpilene ('dipentene') and of its derivatives, which was previously obtained only by the action of heat on isoprene. All of these properties appear to identify this polymer of isoprene with the substance from which isoprene is formed, namely, rubber. The quantity formed is notable and equals possibly one-sixth of the isoprene used."

There is, therefore, no doubt that Bouchardat actually claimed he had prepared an impure synthetic rubber in 1879, and it has frequently been *stated that he was the discoverer of synthetic rubber.*

It is to be remembered, however, that he obtained his isoprene by the dry distillation of natural rubber itself.

In June, 1911, Prof. Harries[1] made the following comment upon this work of Bouchardat:

"It was a bold idea of Bouchardat to directly connect isoprene with rubber, notwithstanding the fact that the dry distillation of rubber yields only extremely small amounts of isoprene." "I have ascertained that only 35 grams of the isoprene fraction, boiling at 33° to 34°, is obtained from $1^1/_2$ kilograms of good rubber."[2] "I also regard it worthy of note that Bouchardat applied the term rubber to the mass resulting by the polymerization of isoprene, although he was deficient in practically all means of proving this statement experimentally. His experiments, as well as those of Tilden, have remained extremely incomplete."

However, I think it should be pointed out that Bouchardat gave an analysis of his product, stated that its elasticity and other properties were similar to those of rubber, mentioned its insolubility in alcohol, its behavior with ether, and its solubility in carbon disulfide as similar to that of natural rubber; and then he claimed to have submitted his product to dry distillation, and obtained the same volatile hydrocarbons as he had previously obtained from natural rubber.

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[1] *Ann.*, 383, 184.

[2] *Gummi-Ztg.*, 24, 853 (March 18, 1910).

In 1910 and 1911, Prof. Harries made use of the tetrabromides, the nitrosities and the ozonides as a means of identifying a sample of rubber. In 1912 and 1913, he finds that these tests are no longer suitable for the identification and comparison of the various rubbers, and he now says that the best method appears to be that of measuring the velocity of decomposition of the diozonides and dioxozonides with water, and the quantitative estimation of the decomposition products. In 1879, Bouchardat had naturally never heard of these tests for rubber, and we can hardly blame him for not employing them. He claimed to have used many of the best tests known at that time, and said he had synthetically prepared an impure rubber.

However, it it quite possible that Bouchardat was mistaken, and that the product which he claimed he had proved to be rubber, really should not be termed rubber at all.

Prof. Perkin, Jr. maintains that Bouchardat's product was an impure, but nevertheless a true rubber. However, Perkin, Jr. apparently relies wholly on Bouchardat's published work and its subsequent confirmation by Tilden. To the best of my knowledge, Perkin, Jr. has never stated that he has repeated Bouchardat's work and obtained true rubber by this method.

On the other hand, Prof. Harries maintains that he has been unable to confirm Bouchardat's work. In his paper[1] published on January 30, 1913, Harries says:

"Perkin again returns to the experiments of Bouchardat and Tilden, who claimed to have polymerized isoprene to rubber by means of hydrochloric acid gas, and he explains, contrary to my statements, that the observations of these investigators are undoubtedly correct.

"On different occasions I have pointed out that Bouchardat and Tilden, if they really did obtain rubber, must have accomplished this result purely by accident; for a large number of chemists have found it impossible to rediscover the conditions needed for the successful performance of this experiment. To those who are familiar with the property of rubber of energetically absorbing hydrochloric acid gas, the possibility of forming pure rubber by action of hydrochloric acid gas upon isoprene seems almost excluded; and further it would be impossible to manufacture a technically useful rubber by this method, because rubber containing hydrochloric acid is crisp or friable."

"Aside from this, I have in the past made numerous experiments in the attempt to polymerize isoprene to rubber by means of hydrochloric acid gas. The chief products of this reaction are always the chlorhydrines of isoprene. After the removal of these chlorhydrines by distillation with steam or by distillation in vacuum, there certainly remains a brown, tough residue. But this residue is for the most part soluble in alcohol, and the most important point is that when this residue is ozonized it never gives a test for levulinic aldehyde. I cannot relinquish the requirement that a product which is to be designated as true rubber, should at least be able to yield this qualitative test.

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[1] *Ann.*, 395, 218

"If Mr. Perkin, Jr. is so much interested in the synthetic preparation of rubber by means of the action of hydrochloric acid gas on isoprene, I beg that he himself try at least once to rediscover the experimental conditions which were hidden by Bouchardat and Tilden. If then, Perkin can so describe the reaction that it may be successfully repeated every time, I will admit without reservation the priority[1] of Bouchardat and Tilden. At the present time I am not in a position to do so, although I appreciate thoroughly the work of these investigators, in so far as I recognize that they gave the hint or suggestion for the later results of Hofmann and myself."

This, at first, did not appear as convincing to me as it might, because every time Prof. Harries mentions this experiment, he speaks of acting upon isoprene with "*Salzsàuregas,*" contrary to Bouchardat's description. Bouchardat never claimed to have prepared his rubber by the action of dry hydrochloric acid *gas* on isoprene; in fact he specifically says that this action does not yield rubber; he did use a solution of hydrochloric acid, made by saturating water at 0° with hydrogen chloride gas, and he states that this concentrated solution of hydrochloric acid acts differently upon isoprene than does dry hydrogen chloride gas.

Through the kindness of Mr. F. G. Achelis of The American Hard Rubber Co., I have been able to repeat this experiment described by Bouchardat. Mr. Achelis very generously supplied me with a suitable quantity of carefully washed and dried fine para rubber which was submitted to a dry distillation. The crude distillate has a rather disagreeable odor, due to the presence of certain volatile bases, which were removed by agitation of the oil with very dilute sulfuric acid, and then with water; the resulting oil was subsequently dried, and finally separated by repeated fractional distillation into several portions, the portion in which we are especially interested boiling at 33° to 60°. By careful and repeated rectifications over sodium, this was then separated into a chief fraction, boiling at 33° to 38°. From 7300 grams of the para rubber, I obtained 176 grams of this isoprene fraction. This fraction is, of course, an impure isoprene, pure isoprene,[2] regenerated from its dibromide by treatment with zinc dust, boiling at 33.5°.

Three portions of 25 grams each of this isoprene fraction were then treated in the cold in sealed pressure bottles with 300, 337.5 and 375 grams, respectively, of a solution of hydrochloric acid saturated at 0°. After agitation, they were allowed to remain at room temperature, one for 15 days, another for $17^1/_2$ days, and the third for 20 days, thus corresponding with Bouchardat's directions, which state that "one part of isoprene was treated in the cold in a sealed vessel with 12 to 15 parts of the acid, and after agitation the whole was left at the room temperature for 15 to 20 days." No rise in temperature of the mixture, as noted by Bouchardat, was observed upon the first agitation. What might be termed a vigorous reaction took place immediately upon agitation, but this seemed to me due to rapid evolution of some of the hydrochloric acid gas from the saturated solution.

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[1] See article by Harries in *Gummi-Ztg.*, **26**, 1408 (June 7, 1912).

[2] Mokiewsky, *J. Russ. Phys. Chem. Soc.*, **30**, 885; **32**, 207.

At the end of the reaction period, the contents of the bottles were added to water and submitted to distillation as long as oily drops were obtained. There remained, with the excess of acid water, only an extremely small, black, tarry residue, which was about as much as one would expect in a steam distillation of any impure oil.

This material was insoluble in alcohol, but readily soluble in ether. It might possibly be termed elastic, but would certainly *not* be called rubber, and it really is only a very inconsiderable residue. The volatile products resulting from the distillation were isoprene mono-hydrochloride and dihydrochloride, and these are certainly the *only* real products which I obtained by the method described by Bouchardat.

Accordingly, I can only say that I failed to successfully repeat Bouchardat's experiment, although I used every precaution to most carefully follow his directions. Personally, therefore, I believe that Prof. Harries and the chemists of Bayer & Co. are quite correct in maintaining that Bouchardat's priority can only be admitted with the reservation that no one since Bouchardat and Tilden has been able to successfully repeat this synthesis, and that it is really important for Prof. Perkin, Jr. or some one else to so describe Bouchardat's experiment that it may be readily and successfully repeated without involving a large amount of research.

In this connection it should be mentioned that Kondakow has offered a possible explanation of these contradictatory results of the various investigators on the Bouchardat synthesis. Kondakow suggests that those chemists who have been unable to confirm Bouchardat's work have used freshly distilled isoprene (and that is certainly true in my own work), and that such isoprene does not give rubber when treated with hydrochloric acid. On the other hand, Bouchardat and Tilden, who claimed to have obtained rubber by treating isoprene with hydrochloric acid, may have used an isoprene which had stood for a long time in the light, and therefore contained more or less of rubber or rubber-like substance dissolved in it. On treating this solution of rubber or a rubber-like substance in isoprene with hydrochloric acid, Bouchardat and Tilden separated the rubber-like substance, and supposed that it had resulted from the action of the hydrochloric acid on the isoprene, whereas as a matter of fact it had been formed by the spontaneous polymerization of the isoprene on standing, before hydrochloric acid was added. Later work by Tilden, Weber, Wallach, and Pickles shows that isoprene on standing is converted slowly (nine months to eight years) into a rubber or rubber-like substance.

If this explanation should prove to be correct, then it might be argued that anyone from Williams in 1860 to the present time, who had made isoprene and allowed it to stand for some time, had unconsciously performed a synthesis of rubber or rubber-like substance, and the latter remained dissolved and unnoticed in the isoprene. Such an assumption might seem to warrant Prof. Perkin, Jr.'s statements that Williams' (1860) product "*undoubtedly contained rubber,*" that Bouchardat's product in 1875 "contained a considerable proportion of rubber," and that Tilden's product made in 1884 by the action of cold acids on colophene, which resulted by the heating of isoprene at 250° to 280° for twelve hours, contained rubber. Such an assumption, however, seems to me rather weak to base such positive statements upon, and is in reality "quite beside the mark."

The next work on synthetic rubber to be considered is that by Tilden, and around this has been waged a rather strenuous debate relative to the amount of credit due to Tilden as a discoverer of synthetic rubber, and as to how far his work anticipated the more recent developments, especially the work of Prof. Harries and of Bayer & Co.

In 1882, Prof. Tilden[1] presented a paper to the Southampton meeting of the British Association, on "Hydrocarbons of Formula $(C_5H_8)_n$." He states:

"Isoprene is said to boil at 37° to 38°, though, according to my own observations, its boiling point is about 3° lower."

"Isoprene presents two characters which distinguish it from the terpenes. One is the peculiar explosive property of the white syrupy substance, which results from its oxidation by air. The other peculiarity—its conversion into true india-rubber or caoutchouc when brought into contact with certain chemical agents, for example, strong aqueous hydrochloric acid as noted by Bouchardat, or nitrosyl-chloride as observed by myself. It is this character of isoprene which gives it a somewhat practical interest, for if it were possible to obtain this hydrocarbon from some other and more accessible source, the synthetical production of india-rubber could be accomplished."

"When turpentine is passed through a red-hot iron tube and the product fractionally distilled, a small quantity of a liquid is actually obtained, having the same composition and some of the properties of isoprene. It boils at about 37°. By the action of concentrated hydrochloric acid it yields a tough substance closely resembling caoutchouc. The small quantity at present in my possession does not enable me to pronounce positively that this liquid is isoprene, but it seems very probable. A liter of turpentine gave about 20 cc. of the fraction from 37° to 40°, or thereabouts. I am engaged in the preparation of a larger quantity, and in the investigation of the somewhat complex series of hydrocarbons which are formed at the same time."

"I incline to the belief that it (isoprene) is β-methylcrotonylene."

The new facts announced in this paper are: (1) Isoprene boils at 34° to 35°. (2) By suitable treatment of turpentine, a 2% yield of a liquid resembling isoprene is obtained. (3) Tilden claims to have prepared true india-rubber by the action of nitrosyl-chloride on isoprene; but no details are given by means of which another chemist could readily confirm his results, and no analyses or properties of the product are mentioned, which would indicate to one reading the paper that this product really was a true rubber. To the best of my knowledge no other investigator has since confirmed this work, and I think that confirmation is desirable and necessary before we can accept it as a scientific fact that *true* rubber is made by acting on isoprene with nitrosyl-chloride. (4) Tilden claims to have prepared "a tough substance closely resembling rubber by the action of concentrated hydrochloric acid" upon *synthetic* isoprene. This is apparently a confirmation and development of Bouchardat's work, inasmuch as the latter used isoprene made from rubber itself, while Tilden used isoprene made from turpentine. No description of the process or properties of the product are given, hence it is impossible for a reader of the paper to say definitely that Tilden's product was real synthetic rubber.

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[1] *Chem. News*, 46, 220.

Prof. Perkin, Jr., characterizes the above paper as "a remarkable tribute to Tilden's intuition that he should not only at this early date have foreseen the successful production of synthetic rubber, but he should also, at the same time, have suggested the correct formula for isoprene."

In 1884, Prof. Tilden published a paper[1] "On the Decomposition of Terpenes by Heat." He states:

"The following is a summary of the results of the examination of the products of the action of heat upon ordinary turpentine oil. 4000 cc. turpentine oil gave 380 cc. of a fraction boiling at 20° to 70°, which yielded about 200 cc. nearly pure pentine." "This liquid boils between 33° and 37°, and smells like isoprene, the pentine from india-rubber." "The formula, C_5H_8, is adopted for this liquid for reasons given hereafter, notwithstanding that the analytical numbers agree with the calculated percentages less closely than could be desired." "Conclusive proof of its composition was obtained by an examination of the polymerisation of this hydrocarbon by heat. A quantity of the fraction 33–35° was sealed up in tubes and heated at 250–280° for about twelve hours. No gas was evolved, but the liquid acquired a slight fluorescence. When submitted to distillation, a quantity of hydrocarbon apparently unaltered was recovered, but about half the volume distilled between 170° and 180°, while a small quantity of pale viscid colophene remained behind." The liquid boiling at 170° to 180° is shown to be dipentene, and is identical with the compounds previously described as diisoprene and terpilene.

"In all probability, also, the pentine from turpentine is identical with isoprene. I have carefully compared them together, and cannot observe any essential difference between them." "Both hydrocarbons absorb hydrochloric acid gas eagerly, giving a mixture of monochloride and dichloride."

"Bouchardat mentions that the action of concentrated hydrochloric acid upon isoprene converts a portion of the hydrocarbon into caoutchouc. This substance is also formed from the turpentine hydrocarbon. It appears to be produced most readily from the oily polymeride, resulting from the action of heat. Contact with strong acids in the cold effects the change." "The pentine obtained from the terpenes is identical with isoprene. This pentine is readily polymerised by heat into terpilene, $2C_5H_8 = C_{10}H_{16}$."

An analysis of this paper shows the following facts:

(1) Turpentine is "cracked" into isoprene by the action of heat, the yield of nearly pure isoprene being about 5% of the volume of turpentine employed. (2) Caoutchouc is said to be formed from this isoprene obtained from turpentine (presumably by the action of concentrated hydrochloric acid upon the isoprene). (3) No analysis or description or properties of this alleged caoutchouc are given. (4) The formation of this caoutchouc was one of the methods used to prove that the isoprene from turpentine was identical with the isoprene formed by the dry distillation

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[1] *J. Chem. Soc. (London)*, **45**, 410.

of rubber. (5) When this isoprene obtained from turpentine is heated in sealed tubes for 12 hours at 250° to 280°, about one-half of it is converted into terpilene or dipentene, a small quantity is polymerized to "pale viscid colophene," and the remainder is unaltered. (6) Tilden claims that rubber "appears to be produced most readily from the '*oily polymeride*,' resulting from the action of heat on isoprene. Contact with strong acids in the cold effects the change."

What does Tilden mean by this "oily polymeride?" Certainly not the unchanged isoprene, hardly the dipentine boiling at 170° to 180°, and therefore it must be the "*pale viscid colophene*." Accordingly, Tilden claims to have synthetically prepared rubber by bringing colophene in contact with strong acids *in the cold.* It seems almost impossible. However, we must bear in mind that Prof. Perkin, Jr. says there is no doubt that the colophene made by Bouchardat in 1875 by heating isoprene in sealed tubes at 280 290° "contained a considerable proportion of rubber," and therefore Tilden's colophene made in a similar manner might be expected to contain rubber, even before it came in contact with cold acids. Moreover, in referring to this paper, Prof. Perkin, Jr. says:

"In confirmation of Tilden's results, Lilley, by heating isoprene, recently obtained a body which he called 'mesoprene' (clearly Tilden's 'oily polymer'), and showed that this may be converted into rubber by the action of acid or other agents." And again Perkin remarks:

"On December 14, 1909, G. Lilley, working in England, took out the patent[1] to which I have already referred for making 'mesoprene' by the action of heat on isoprene, and then acting upon the oily polymeride thus formed, with acids, etc. We have seen samples of the rubber made in this way and their formation by this process completely vindicates Tilden's early statements, if such vindication were necessary."

The Lilley patent, cited by Perkin, Jr. in confirmation and vindication of Tilden's statement, is on "The Production of Synthetic India-Rubber or Rubber-like Material." It states:

"'Mesoprene' is the name given to a product obtained by heating the 'basic principle of india-rubber' or a body containing the same at a temperature below 200° under pressure, either alone or in presence of some added substance or substances, such as (1) mesoprene, (2) alcohol, or other rubber precipitant, (3) a liquid hydrocarbon mixture, obtained as a by-product in the production of mesoprene, (4) an acid. The 'basic principle' may be treated with air or oxygen before subjecting it to the action of heat. Any unconverted substance is removed by distillation, the residue in the still constituting mesoprene, which is free from water by drying *in vacuo* at ,100°. The distillate, or a portion of it, constitutes the liquid hydrocarbon mixture referred to under (3) above. The 'basic principle of india-rubber' is obtained by subjecting the vapour of turpentine or a selected fraction or fractions of the distillates from the crude turpentine exudation to a temperature of about 500-600°, condensing the products and separating the more volatile constituents by fractionation, preferably selecting the portions distilling below 90°, in which isoprene and other hydrocarbons suitable for the purpose of the invention are present.

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[1] Eng. Patent, 29,277. Date of application Dec. 14, 1909; accepted Mar. 14, 1911; *J. Soc. Chem. Ind.*, 30, 561; *C. A.*, 5, 3173 (1911).

"The synthetic india-rubber, or rubber-like body, is produced by heating 'mesoprene,' prepared as above described, either alone, or by floating it on water heated to 100°, or in the presence of sulfuric acid or its decomposition products, or hydrochloric acid, or sulfur dioxide which may be passed through the dry heated mesoprene."

This is a very interesting patent in some respects, but I still fail to see how it vindicates or confirms Tilden's statement that "*contact with strong acids in the cold effects the change*" of colophene (made by heating isoprene at 250–280°) into rubber. For so-called "mesoprene," *made by heating oxidized or ozonized isoprene and other hydrocarbons suitable for the purpose at a temperature below 200°, with alcohol and an acid,* is not necessarily the same as colophene made by heating isoprene alone at a temperature of 250° to 280°.

Therefore, I believe Tilden's statement—that the contact of pale, viscid colophene with strong acids in the cold, produces rubber—needs accurate confirmation. As a matter of fact, later statements[1] made by Tilden in 1906 and 1908 show that when he tried to make rubber from isoprene "by heat or contact with strong reagents, the greater part of the hydrocarbon is converted into dipentene and the mixture of viscid compounds of high boiling point known as colophene, which results from the polymerisation of the terpenes." There is no intimation that the strong reagents then converted this colophene into rubber.

In this connection, and bearing direct testimony upon the question as to whether colophene does or does not contain rubber, it is interesting to again quote from Harries' recent paper.[2] He says:

"While engaged with the problem of the conversion of isoprene into rubber, I made many experiments to bring about the polymerisation of this hydrocarbon by means of catalytic agents. The resulting product was then always at first ozonized to see whether it gave the pyrrol test. the results showed that most of the oils and resins (colophene), which were obtained, did not give this test, and therefore had nothing to do with rubber."

Again referring to this paper by Tilden, Prof. Perkin, Jr. says: "This paper is of special interest since we have here the first possibility of the commercial manufacture of rubber."

In 1908, Tilden is reported as saying, relative to the commercial manufacture of rubber from isoprene made from turpentine:

"If isoprene were obtainable at a low cost from other sources, it might be found possible to utilize the hydrochloric acid process, though I doubt it."

And again on December 11, 1912, in the discussion of Dr. F. M. Perkin's lecture, Sir William Tilden said:

"The key to synthetic rubber was provided by the discovery made by Dr. Matthews, of the remarkable action of the metal sodium. Without some such method for rapidly producing polymerisation it would be impracticable with the amount of isoprene, or other hydrocarbon, to come within measurable distance of producing rubber for practical purposes."

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[1] Report of the British Association for the Advancement of Science, 1906, York. Transactions of Section B, page 525.

[2] *Ann.*, 395, 220.

In his second paper[1] "On the Terpenes," dated December 19, 1884, Wallach refers to the heat polymerisation of the isoprene obtained by the dry distillation of rubber, with these words:

"Isoprene has recently been investigated by Bouchardat and Tilden with very interesting results. Both agree that on heating, isoprene is polymerized to a hydrocarbon, $C_{10}H_{16}$, which is identical with caoutchine. *I can confirm these statements in every respect.*

"When isoprene is heated for some hours at 250° to 270°, there is formed, together with high boiling polymerization-products, a hydrocarbon boiling at 180°, which has been identified by its tetrabromide as caoutchouc or di-isoprene, and this is identical with cinene."

In 1886 Wallach[2] tried various methods for the polymerisation of the isoprene obtained by the distillation of rubber. He mentions incidentally:

"When isoprene is placed in sealed tubes and is exposed to the action of light for a long time, a product is formed which, when treated with alcohol, forms a tough mass, resembling rubber; this material became more or less hard on exposure to air."

Nothing more is said about this product.

On May 18, 1892, Prof. Tilden read a paper[3] before the Philosophical Society of Birmingham on "The Spontaneous Conversion of Isoprene into Caoutchouc." I quote the following from this paper:

"Bouchardat observed that when isoprene is heated to a temperature near 300°, it gradually polymerises into a terpene which he called di-isoprene, but which is now usually called *dipentene*. This compound boils at 176°. A quantity of colophene similar to that which is produced by the action of heat upon turpentine is formed at the same time,

"When isoprene is brought into contact with strong acids, aqueous hydrochloric acid for example, it is converted into a tough elastic solid, which has been examined by G. Bouchardat and by myself; it appears to be true india-rubber.

"Specimens of isoprene were made from several terpenes in the course of my work on those compounds, and some of them I have preserved. I was surprised a few weeks ago at finding the contents of the bottles containing isoprene from turpentine entirely changed in appearance. In place of a limpid colourless liquid the bottle contained a dense syrup, in which was floating several large masses of solid of a yellowish colour. Upon examination this turned out to be india-rubber. The change of isoprene by spontaneous polymerisation has not to my knowledge been observed before. I can only account for it by the hypothesis that a small quantity of acetic or formic acid had been produced by the oxidising action of the air, and that the presence of this compound had been the means of transforming the rest. The liquid was acid to test paper, and yielded a small portion of unchanged isoprene.

"Synthetic india-rubber, like natural rubber appears to consist of two substances, one of which is more soluble in benzene or in carbon bisulphide than the other. A solution of the artificial rubber in benzene leaves on evaporation a residue which agrees in all characters with a similar preparation from para rubber. The artificial rubber unites with sulphur in the same way as ordinary rubber, forming a tough elastic compound.

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[1] *Ann.*, **227**, 295.

[2] *Ibid.*, **238**, 88.

[3] *Chem. News*, **65**, 265 (1892).

"The constitutional formula of isoprene is not known with certainty, but it must be selected from the five following formulae." Three of these formulas represent derivatives of allene, and two are derived from crotonylene.

"It is obvious that compounds such as these containing doubly-linked carbon may polymerise in a variety of ways, and in the present condition of our knowledge of the constitution, even, of isoprene, it would be idle to speculate as to which one of the numerous possible arrangements would correspond to the constitution of caoutchouc."

The important facts presented in this paper are: (1) Heat polymerizes isoprene to dipentene and colophene, the latter being similar to that formed by the action of heat on turpentine. (2) Tilden confirms Bouchardat's work on the conversion of isoprene into a tough elastic solid, which appeared to be true india-rubber, by the action of aqueous hydrochloric acid; no description of the product is given. (3) The spontaneous polymerization of isoprene into rubber or a rubber-like substance in the course of eight years is noted. (4) Some properties of this synthetic rubber are given, such as its solubility in benzene and carbon disulfide, its color, elasticity, and the fact, that it combines with sulfur like natural rubber. This is noteworthy, because in his papers on the polymerization of isoprene to rubber-like substances, Tilden rarely gives much information regarding the properties of his products.

This important discovery by Tilden of the spontaneous polymerization of isoprene to rubber, or a rubber-like substance, was soon corroborated by Dr. C. O. Weber, and some eighteen years later was confirmed by S. S. Pickles. Therefore, to Tilden belongs the entire credit of having prepared rubber, or a product closely resembling rubber, for the first time, by the slow spontaneous polymerization of synthetic isoprene, and he apparently had synthetic rubber, or something very similar to it, in his hands as early as 1892.

Regarding Tilden's previous work on rubber, I think we shall have to agree with Prof. Harries when he remarks that Tilden's experiments on rubber were certainly *extremely incomplete*.

A paper[1] of interest and importance in this case, and one which bears direct testimony regarding Tilden's synthesis of rubber in 1892 by the slow polymerization of isoprene, was read by C. O. Weber before the Manchester Section of the Society of Chemical Industry, on January 5, 1894.

I quote the following from this paper:

"Tilden obtained isoprene by distilling turpentine through porcelain tubes at a dull red heat, and discovered subsequently that this compound, on standing, spontaneously polymerises into india-rubber. I am in a position to confirm this observation with respect to isoprene obtained from india-rubber by dry distillation. About 300 grams of this substance were found after nine months' standing to be converted into a very viscid, treacly mass, from which by treatment with methyl alcohol, a solid spongy substance of almost white colour could be separated. This substance, after drying, was of a light brown color, and in all respects identical with india-rubber. The weight of india-rubber thus obtained was 211 grams.

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[1] *J. Soc. Chem. Ind.*, 13, 11 (1894).

"Whether in the future we shall succeed to manufacture india-rubber artificially by means of isoprene appears very doubtful as yet. The manufacture of cheap isoprene is certainly an exceedingly difficult task to start with, and on the other hand we have not succeeded so far to completely polymerise it into india-rubber. The by-products of this polymerisation consist of dipentene and polyterpenes, which will always remain comparatively worthless, there being any amount of cheap natural terpenes. At the present time the constitution of isoprene itself is very doubtful."

Regarding the constitution of rubber, Weber says:

"All these condensation products of isoprene are terpenes or polyterpenes, and the fact that the results of the analysis of india-rubber lead to the empirical formula, $C_{10}H_{16}$, which is that of the terpenes, might induce us to pronounce also india-rubber a terpene, or possibly a polyterpene $(C_{10}H_{16})_n$. What we know with certainty is the formation of india-rubber from isoprene by polymerization, and we further know that the molecular weight of it is much higher than $C_{10}H_{16}$. Under these circumstances it appears very much preferable to describe india-rubber as a polyprene $(C_5H_8)_n$."

In this paper, Weber gives the yield of his product, stating that he obtained a little more than two-thirds of the weight of the isoprene used. He also gives the time required to accomplish the spontaneous polymerization of isoprene to his rubber, *viz.*, nine months; this seems like an extremely short time, for the testimony of other investigators is that it requires several years to accomplish this spontaneous change. Thus, judging by the dates of Tilden's papers, he found the change to have taken place after seven or eight years. In a more recent article, Pickles states that when isoprene is allowed to stand for 3$^1/_2$ years it is only incompletely converted into an immature rubber. Hence, Weber must have happened upon conditions which were not met with by the others.

Unfortunately, Weber gives no analyses or specific properties by which he identified his synthetic rubber; he simply states that his product was "in all respects identical with india-rubber," and some will agree that he was qualified to know about it, and will accept his word that he had synthetic rubber in his hands prior to the year 1894. Others will be within their rights and can scarcely be regarded as unreasonable, if they maintain that Weber may possibly have prepared a rubber-like substance, but that he gave no proof which can be regarded as establishing as a scientific fact that he actually prepared synthetic india-rubber.

In 1910, S. S. Pickles published a paper[1] on "The Constitution and Synthesis of Caoutchouc" in which he confirms Tilden's and Weber's spontaneous polymerization synthesis. Under the heading "Spontaneous Polymerisation of Isoprene and Examination of the Product," Pickle says:

"In view of the position of the subject at the present time, the author considered that an account of the result of a recent experiment on the polymerisation of isoprene might have some little value, especially as chemical tests were applied to the product obtained. The difficulty so far as repetition is concerned lies in the fact that the process of spontaneous polymerisation is an extremely slow one, the complete conversion requiring several years.

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[1] *J. Chem. Soc.*, 97, 1086 (1910).

"In 1906, the author prepared a specimen of isoprene (about 10 grams for demonstration purposes), from plantation biscuit rubber; it boiled at 35° to 37°. The small bottle containing it was almost full, the stopper was securely fastened down, and the specimen was allowed to remain in that condition (for the greater part of the time in the dark) for three and a half years. The liquid, which at first was as mobile as ether, had, during this period, gradually become more viscous, until it acquired the consistency of a thick syrup. A short time ago a portion of this liquid was poured out, and to it was added about 10 volumes of alcohol. The separation of a white substance, followed by a clotting, took place immediately. The coagulum thus formed was washed with alcohol and allowed to dry on a glass plate. As thus prepared, the material was clear, gelatinous, and possessed of a certain amount of elasticity. In point of tenacity however i was certainly not equal to mature Para rubber, but rather resembled the product obtained from young, immature rubber trees. It should be remembered, however, that in the experiment the polymerisation had not been allowed to proceed to completion, that is, until reaching the completely solid state. That the material undoubtedly contains rubber, however, is proved by the fact that it yields the characteristic tetrabromide and the nitrosite."

This would seem to unquestionably confirm Tilden's synthesis of rubber by the slow spontaneous polymerization of isoprene, and prove that he had a true synthetic rubber in 1892.

However, in his last paper[1] on this subject, Prof. Harries describes certain investigations on the rubber-like products obtained from β,γ-, or 2,3-dimethylbutadiene, which seem pertinent at this point. He finds that the normal dimethylbutadiene rubber, prepared according to the Elberfeld method of heating dimethylbutadiene for some time in closed tubes, and the white, solid, practically insoluble mass, which Kondakow obtained by allowing dimethylbutadiene to stand in closed tubes for about a year at the ordinary temperature, are different in physical and chemical properties. In this connection Harries says:

"The product obtained by polymerizing dimethylbutadiene at elevated temperatures is apparently different from the product obtained by its slow, spontaneous polymerization in the cold; the latter is absolutely not a true rubber. The determination of this fact appears to me of great importance, because it naturally follows from this that isoprene, and the butadiene hydrocarbons in general, will yield a different product by the slow, spontaneous polymerization in the cold, than by the polymerization at elevated temperatures. Hence, the proof recently advanced by Pickles,[2] that isoprene is converted into rubber by long standing in the cold, is uncertain, because the products of cold polymerization also yield bromides and nitrosites which are difficult to distinguish from those obtained from the heat-polymerization products.

"In order to study this question somewhat more closely, I placed some pure isoprene in a quartz-glass tube, sealed it, and exposed it to the action of the ultraviolet rays for 20 days and nights. At the end of this time, I obtained a white, solid product, which possesses great similarity with the product obtained by Kondakow by the cold polymerization of dimethylbutadiene. This product is tough at first, later becoming brittle, and is absolutely insoluble. Together with this insoluble product, there was formed a small amount of a rubber-like substance, which in my opinion was formed by the unavoidable heating of the isoprene by the lighting process. Unfortunately the quantities of the substances formed were too small to permit of closer investigation."

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[1] *Ann.*, **395**, 265.

[2] *J. Chem. Soc.*, **97**, 1085 (1910).

This, then, appears to reopen the question, does the slow, spontaneous polymerization of isoprene at ordinary temperatures produce a true rubber? Tilden, Weber, Pickles, and Perkin, Jr. are on record in the affirmative; Harries inclines to the negative.

At a meeting of the British Association for the Advancement of Science held at York in 1906, Prof. Tilden submitted a paper[1] "On the Polymerisation of Isoprene." He says:

"When kept for a long time isoprene is slowly converted into india-rubber, the process, however, occupying many years. The specimens now exhibited illustrate the process of transformation. If any attempt is made to hasten the operation, as by heat or contact with strong reagents, the greater part of the hydrocarbon is converted into dipentene, and the mixture of viscid compounds of high boiling-point known as colophene, which results from the polymerisation of the terpenes."

The next important reference concerning Prof. Tilden's work on synthetic rubber is found in the *India-Rubber Journal*,[2] published in the year 1908. I quote the following from an article in this Journal:

"In a letter once published in the 'Kew Bulletin,' the learned and enthusiastic Professor (Tilden) stated that: 'As you may imagine I have tried everything I can think of as likely to promote this change (of isoprene into rubber), but without success. The polymerisation proceeds *very slowly*, occupying according to *my experiences several years*, and all attempts to hurry it result in the production, not of rubber, but of colophene, a thick, sticky oil, quite useless for all purposes to which rubber is applied "

Statement for *India-Rubber Journal* readers:

"Professor Tilden has courteously sent in the following letter which embodies the result of his researches up to date, and his opinion of the future possibilities of synthetic rubber, for publication in the 'India-Rubber Journal.' We have not yet met a manufacturer (and we never expect to meet a planter) who hails the possible advent of a commercial synthetic rubber with any symptoms of joy; the Professor's letter will therefore be followed with unmixed pleasure by our readers. He writes:

" 'The conversion of isoprene into rubber occurs, so far as observed, under two conditions: (1) When brought into contact with strong aqueous hydrochloric acid or moist hydrogen chloride gas; (2) by spontaneous polymerisation. In the former case the amount of rubber produced is small, as it is only a by-product attending the formation of the isoprene hydrochlorides which are both liquids. *In the latter case the process oc-*

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[1] Report of the British Association for the Advancement of Science, 1906, York. Transactions of Section B, page 525

[2] *India-Rubber J.*, 36, 321–322 (1908); *Gummi-Ztg.*, 23, 151 (Nov. 6, 1908); see also *Ann.*, 383, 185; "Die Synthese der Kautschuks," by Ditmar, page 24.

cupies several years. Of course, many attempts were made by me to hasten the process, but it was found that contact with any strong reagent, such as oil of vitriol, pentachloride of phosphorus, and others of milder character, led only to the production of a sticky colophene similar to the substance which results from the polymerisation of the terpenes, and after a course of experiments which were carried on for about two years, I was reluctantly obliged to abandon the subject. *It is, however, a question whether the process could be made commercially productive even if a suitable reagent could be found to effect the transformation, because the yield of isoprene from turpentine is very small, probably not exceeding 10% under favorable conditions. In my experiments it was less. If isoprene was obtainable at a low cost from other sources it might be found possible to utilize the hydrochloric acid process, though I doubt it.*'"

No better summary of Prof. Tilden's work on synthetic rubber could be given than he himself gives in this article, published a few years before the controversy regarding his work commenced. It is interesting to note that he makes no claim that his colophene contained a "considerable proportion of rubber," or that cold acids converted this "oily polymeride" into rubber. It is needless to say that this article by Tilden does not fit in any too well with Prof. Perkin's argument, and in his paper of 1912 in the *Journal of the Society of Chemical Industry* he omits all reference to it. It is likewise apparent that this statement by Tilden pleases the German investigators and they quote it.

This brings us up to the year 1909, the date of the first patents of Bayer & Co., Elberfeld, on the heat polymerisation of isoprene and of other butadiene hydrocarbons to synthetic rubbers.

For the sake of a clear understanding of some subsequent developments, I desire to quote certain portions of Bayer & Co.'s first German patent application,[1] dated September 11, 1909, on "A Method for the Preparation of Artificial Rubber." The patent says:

"An observation of exceedingly great importance technically has been made in the discovery of the fact that by heating synthetic isoprene, a very good yield of a product is obtained, which, in its chemical and physical properties, cannot be distinguished from natural rubber."

"With our process, the temperature may vary within fairly wide limits, but if it greatly exceeds 200° large amounts of terpenes are readily formed. In carrying out the reaction, the synthetic isoprene may be heated in the presence of indifferent diluting agents or solvents, or in the presence of neutral, alkaline or acid catalysts.

"Example 1. 200 parts of isoprene are heated in an autoclave at 200° for 10-12 hours, when a very tough and elastic, but sticky mass is formed. The stickiness is removed by passing steam through the mass, and there results a substance which cannot be distinguished from natural rubber.

"Example 2. 500 parts of isoprene are warmed in a pressure-vessel at 90–100° for six days. The resulting viscous mass is then distilled with steam at ordinary pressure until all unchanged isoprene is driven over. Then, the steam distillation is continued under diminished pressure until no more oil comes over. On cooling, a pure, white rubber of excellent quality remains in the distillation apparatus.

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[1] Deutsche Patentanmeldung F. 28390, Kl 39 b. Gr. 1, vom 11, Sept., 1909. Von den Farbenfabriken vorm. Friedr. Bayer & Co., Elberfeld.

"Example 3. 100 parts of isoprene are dissolved in 200 parts of benzene, and the solution is heated under pressure at 120° for two days; the product is then distilled, first at ordinary pressure and finally in vacuum. Unaltered isoprene, benzene, and terpenes pass over first, and a tough, transparent mass remains, which, after washing with alcohol, loses its transparency, and assumes the outward appearance of rubber.

"*Patent Claim. A process for the preparation of artificial rubber, which consists in heating synthetic isoprene, with or without the addition of agents promoting polymerisation, at a temperature under 250°.*"

In his address before the London section of the Society of Chemical Industry on June 17, 1912, Professor Perkin, Jr., says:

"I should like next to call attention to a German application (H44,823) lodged in October, **1908**, by A. Heinemann, but apparently not published until September, 1911. This patent (corresponding to the English patent, 21,772/07; see THIS JOURNAL, **1908**, 1075) describes the method of heat polymerisation of isoprene as follows:

"'This hydrocarbon contains two double bonds and so is easily polymerised. This follows in known manner by heating in a sealed tube with or without the addition of acids, alkalis or neutral catalysts. The temperature is preferably kept at 100° to 150° for three days. Higher or lower temperatures work in a shorter or longer time than three days. After polymerisation, a rubber-like mass is obtained, in solution in unpolymerised hydrocarbon or hydrocarbon polymerised only to an oil. The hydrocarbon can be separated by distillation or by the known methods of precipitating natural rubber.'"

Perkin, Jr., continues as follows: "Meanwhile, the Bayer & Co. had been at work on the problem and filed an English patent, 17,734/10 (see THIS JOURNAL, **1911**, 226), dated September 11, 1909, and a French patent, 419,316, the first of a series of patents for the heat polymerisation of isoprene and its homologues. The gist of these patents is very well described by Heinemann's remarks, which I have just quoted, and they do not appear to contain much which was not known before."

If Perkin's statements are correct and his conclusion is justified, then we are allowed to infer that the chemists of Bayer & Co., by some strange coincident, applied for a patent, in which they described their discovery in nearly the same language which Heinemann had one year previously used in a patent application to describe the same discovery. If Perkin's statements were based upon insufficient information, and the facts are not as he stated, then, it seems to me, an injustice has been committed against the chemists of Bayer & Co.

In a short article[1] in "Gummi-Zeitung," for August 9, 1912, Dr. Fritz Hofmann, of Elberfeld, replies to this statement by Perkin, Jr., in the following words:

"The Heinemann application H44,823 was definitely or finally rejected by the German patent office in May, 1912. This application as a matter of fact did contain the parts quoted by Perkin, but these particular parts were never contained in the original application filed in October, 1908. Furthermore, the parts quoted by Perkin are not contained in Heinemann's English patent, 21,772/07, nor are they to be found in

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[1] *Gummi-Ztg.*, **45**, 1794 (1912). See also *Ibid.*, **26**, 1458 (June 14, 1912); **26**, 1752 (Aug. 2, 1912).

Heinemann's French patent, 394,795. In the German application, H44,823, the part quoted by Perkin was first introduced as an addition on December 14, 1910, that is, at a time when the heat polymerisation of isoprene had become generally known through the well-known Vienna lecture of Prof. Harries on March 12, 1910, and by the French application of the Badische Anilin- und Sodafabrik—made public on November 8, 1910. The basic patent of the Farbenfabriken vorm. Friedr. Bayer & Co., which for the first time described the heat polymerization and patented this discovery, was delivered at the Imperial patent office on September 11, 1909."

On investigation, I find the facts relative to Heinemann's English patent, No. 21,772, which Perkin, Jr., mentions as corresponding with the German application, are as follows:

Date of application, October 2, 1907. Accepted October 1, 1908. Subject, "A Process for the Synthetic Production of India-Rubber," by Arthur Heinemann of London. The discovery is given as follows: "Acetylene and ethylene are mixed together and heated in a tube or the like raised to a dull red heat, thus producing divinyl. The divinyl is then converted into methyl divinyl or isoprene in any well-known manner, such for instance, as by the action of methyl chloride, or by passing the three gases together through said tube. The methyl divinyl or isoprene resulting from the last reaction is then treated with concentrated hydrochloric acid and condensed to caoutchouc."

"Caoutchouc prepared by the above described method is as good as the natural product, with which it can compete."

There is absolutely no reference in this patent to the heat polymerization of isoprene.

Heinemann's French application,[1] dated September 30, 1908, is exactly like the English patent and contains no reference to the heat polymerization of isoprene. These patents deal with an alleged process of preparing synthetic isoprene and then polymerizing this by Bouchardat's method.

The abstract in the *Journal of the Society of Chemical Industry* for 1908, to which Perkin, Jr., refers, gives a very short notice of Heinemann's English patent, saying that isoprene is formed from acetylene, ethylene and methyl chloride, and that the resulting isoprene is condensed to rubber; but absolutely no mention is made of the condensing or polymerizing agent, nor of heat polymerization.

Regarding Heinemann's German application, H44,823, dated October 1, 1908, I find this printed in Dr. Rudolf Ditmar's monograph on "The Synthesis of Rubber," the preface of which is dated March, 1912. As printed in this book, the German application includes the heat polymerization of isoprene as quoted by Perkin, Jr. If one used this book in this connection, there would be some reasons for believing that the German application, dated October 1, 1908, anticipated Bayer & Co.'s 1909 patent. However, in the part of the patent application relating to the polymerization of isoprene, as quoted by Perkin, Jr. there is one phrase which would be looked upon with *surprise*, at least, by those familiar with the history of synthetic rubber, and that is: The polymerization of isoprene to rubber "follows in *known manner* by heating in a sealed tube with or without the addition of acids, alkalies, or neutral catalysts."

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[1] *C. A.*, 4, 2746 (1910).

On October 1, 1908, the date Perkin, Jr., assumes this to have been presented to the German patent office, and indeed up to September 11, 1909, the *known methods* of polymerizing isoprene were: (1) Bouchardat's, Tilden's, and Wallach's experiments of heating isoprene in sealed tubes at 250° to 290°, when dipentene and a mixture of diterpenes termed colophene were formed, but no rubber was mentioned by these investigators. (2) Bouchardat's and Tilden's work in treating isoprene in the cold with strong aqueous hydrochloric acid, which gave a small yield of a product which they termed synthetic rubber. (3) Wallach's, Tilden's and Weber's experiments on the slow, spontaneous polymerization of isoprene at ordinary temperatures to a rubber-like product.

If this part in Heinemann's German application was really written prior to October 1, 1908, then Heinemann's process of heat ploymerisation of isoprene to rubber was a new discovery of great importance, and it is remarkable that he should term it a "*known method.*"

Furthermore, there is no reason to doubt Dr. Hofmann's word regarding this patent situation, and I think we are not warranted in assuming that the "gist" of the Bayer & Co. patent was described by Heinemann in 1908.

This brings us up to the time of the Bayer & Co. and Prof. Harries' patents and publications, and it may be regarded as the close of the first period in the history of synthetic rubber.

We may, therefore, summarize the pioneer work on the polymerization of *isoprene* to rubber, *i. e.*, the work published up to about September 11, 1909, as follows:

1. A synthetic rubber was first claimed by G. Bouchardat in 1879 by polymerization of isoprene in the cold by means of strong aqueous hydrochloric acid. This synthesis is said to have been confirmed by Tilden in 1882 and 1884, and by A. Heinemann in 1907. It has been denied by Professors Klages and Harries, and by Bayer & Co., and has been defended by Prof. Perkin, Jr., who has not, to my knowledge, stated that he himself ever made true rubber by this process.

(2) In 1882 and 1884, Professor Tilden claimed to have produced rubber by the action of nitrosyl-chloride on isoprene, and by the action of *cold* acids on the "oily polymeride," colophene, produced by heating isoprene at 250° to 280° for about twelve hours. To the best of my knowledge, neither of these syntheses has been confirmed by any other investigator.

(3) Bouchardat, in 1875, and Tilden and Wallach in 1884, all agreed that heating isoprene in sealed tubes at 250° to 290° for several hours, converted it into dipentene and colophene; the *formation of rubber under these conditions was not noted by these investigators.* Prof. Perkin, Jr claims "there can be no doubt that this colophene contained a considerable proportion of rubber."

(4) In 1886, Wallach noted that when isoprene was exposed to the action of light for a long time, a tough mass, resembling rubber was formed. This product was apparently not further investigated.

(5) In 1892, Prof. Tilden discovered the spontaneous polymerization of isoprene to rubber or a rubber-like substance, the process requiring a number of years for its completion. This synthesis has been confirmed by Weber and Pickles, but the question as to whether this product should be regarded as a true rubber has been raised by Prof. Harries.

(6) On September 11, 1909, Bayer & Co. patented their first process for the preparation of artificial rubber, consisting in heating synthetic isoprene with or without the addition of neutral, alkaline, or acid catalysts, at a temperature under 250°. In my opinion, there is absolutely nothing in the prior state of the art, which can be regarded as anticipating this discovery of the chemists of Bayer & Co.

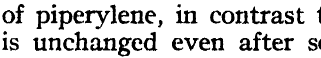
So far we have considered the early history of the polymerisation of isoprene only. A few words should be added regarding what was known to the earlier investigators about the polymerisation products of isomers and homologues of isoprene, because it has been intimated that the polymerides obtained from these substances, in their behavior with solvents and in certain of their properties, showed a general resemblance to the properties of rubber. It is also clear that those who call our attention to these polymerization products, permit us to infer that this alleged resemblance to rubber should, in some way, anticipate the work of Prof. Harries and Bayer & Co. But we should remember that this class of unsaturated compounds are readily polymerized or resinfied; and we know that in working with organic compounds, we have obtained tarry or resinous products which we may have termed gummy or rubber-like, but which we never dreamed of having any real relationship with true india-rubber.

We will first consider *piperylene*, an isomer of isoprene. In 1881, Hofmann[1] examined piperylene. He says: "The boiling point of this substance is about 42°; towards the end of this distillation, the temperature rose somewhat, so that possibly the polymerization of a small amount may be indicated."

In 1882, Schotten[2] tried to prepare piperylene from nitro-piperidine. He says: "I have found that on heating with phosphoric anhydride, as well as with zinc chloride, only traces of piperylene are formed, and that the mass is largely resinfied (verharzt)."

I mention the above two references because Prof. Perkin, Jr.[3] calls attention to these as indicating that Hofmann and Schotten "obtained similar polymerides," and that here "we find the first example of the polymerization of a homologue of isoprene."

In 1901, J. Thiele[4] published a paper on piperylene. I quote the following from this paper: "Piperylene has the constitution of an α-methylbutadiene,



$$CH_2 = CH - CH = \underset{\displaystyle CH_3}{\underset{|}{CH}}$$

"The boiling point of piperylene, in contrast to that of the β-methylbutadiene (isoprene), is unchanged even after several months' standing in the dark, and as a residue there remains only a minimum amount of a gummy (gummiartigen) substance, probably a polymerisation product."

Prof. Perkin, Jr.[5] in using this reference says: "In 1901, Thiele showed that on keeping, it (piperylene) yielded a small quantity of a rubber like polymer, but not so readily as isoprene does."

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[1] *Ber.*, 14, 665.

[2] *Ibid.*, 15, 425.

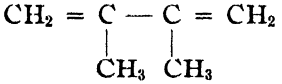
[3] *J. Soc. Chem Ind.*, 31, 617.

[4] *Ann.*, 319, 227.

[5] *J. Soc. Chem. Ind.*, 31, 618.

We must keep in mind, however, that Thiele used the word "gummiartigen" and not "kautschukartigen."

Another compound to which our attention has been called is 2,3-dimethylbutadiene, or as it has frequently been termed, dipropylene or diisopropenyl,



$$CH_2 = \underset{CH_3}{\underset{|}{C}} - \underset{CH_3}{\underset{|}{C}} = CH_2$$

In 1890, Marintza[1] stated: "Dimethyl isopropenyl carbinol was subjected to the action of sulfuric and hydrochloric acids. When it was heated at 100° with dilute sulfuric acid (containing 1% or more), the product was a viscid oil, boiling above 100°, seemingly the product of condensation of a hydrocarbon (diisopropenyl) formed by the action of very dilute acids.

"After heating for 20 to 30 minutes in a water bath with hydrochloric acid of 0.1% a very mobile, liquid hydrocarbon, boiling at 68° to 69°, was obtained. The hydrocarbon is C_6H_{10}, diisopropenyl."

In 1892, F. Couturier[2] writes: "β-dipropylene polymerises with extreme ease, which does not take place with the isomeric compounds having the normal chain, such as diallyl. This property renders all of the reactions with this hydrocarbon very difficult. The polymerization is produced by heat alone, and the liquid is transformed into a viscous product, which cannot be distilled. Calcium chloride acts in the same manner in the cold, when it is allowed to stand in contact with the hydrocarbon for a long time."

"I have tried to hydrate β-dipropylene by means of sulfuric acid. But this attempt was rendered fruitless by the extreme ease with which this hydrocarbon polymerises. When the hydrocarbon is added to sulfuric acid, cooled to zero, the liquid becomes colored and viscous. When the product is cooled with ice, there separates a resinous material, which agglomerates and which yields no volatile products when distilled with steam. This resinous product is soluble in ether, chloroform, acetic acid, and benzine; but none of these solvents gave a product suitable for analysis."

Referring to the above article, Perkin, Jr. says: "In 1892, Couturier added another member to the rubber series, since he found that diisopropenyl (dipropylene) polymerises very readily, *e. g.*, by the action of heat." Perkin, Jr: adds that the agglomeration and the solubilities of Couturier's "resin" are "properties somewhat resembling those of freshly precipitated rubber."

The fact nevertheless remains that Couturier does not intimate that his resinous product is even remotely related to rubber, and personally I do not see how *his* work added "another member to the rubber series."

In 1900, Kondakow[3] investigated the behavior of diisopropenyl towards alcoholic potash, in order to determine whether this hydrocarbon is polymerized under these conditions. He says: "When this hydrocarbon is heated with alcoholic potash (1 part potassium hydroxide to 3 parts of alcohol) at 150° for five hours, a part of the hydrocarbon is polymerised, and the remainder is unaltered. The remaining, unaltered portion of the diisopropenyl boils at 69.5° to 70°."

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[1] *J Chem Soc, Abstr* **58**, 728 (1890) (from *J Russ Chem Soc*, **21**, 434)

[2] *Ann. chim. phys*, **26**, 489, 491

[3] *J. prakt. Chem.*, **62**, 175, 176.

"As regards the polymerisation product which is obtained by heating diisopropenyl with alcoholic potash, its properties recall those of caoutchouc or of the polymer of styrene. The product is a leather-like, elastic mass, nearly white in color, is not volatile with steam, is insoluble in water, but is soluble in hydrocarbons, ether and alcohol."

In 1901, Kondakow[1] published a short paper on "A Remarkable Case of Polymerization of Diisopropenyl (Dimethyl-2,3-butadiene-1,3)." He placed two lots of 20 grams each of diisopropenyl in two 50 cc. flasks, the flasks being about two-fifths full of the liquid. "The flasks were then sealed and allowed to stand in diffused daylight for about one year. At the end of this time, the liquid was found to have been converted into a white solid mass, which completely filled the flasks in the form of a sponge. On opening the flasks, neither increase or decrease in pressure was observed and no trace of the original hydrocarbon was found Under the microscope the substance seemed to be amorphous, and it is tasteless and odorless, and elastic like rubber; it also reminds one of rubber in its behavior on chewing, and it appears to be unchanged in the air. The substance is absolutely insoluble in benzine, ligroin, ligroin chloroform, carbon disulfide, ether, alcohol, acetone and turpentine; it swells up in benzene. It is distinguished from rubber by its behavior towards these solvents."

Then Kondakow adds: "I can only point out that the second polymer is clearly or sharply distinguished from the previously described polymer (the one soluble in alcohol) by its physical properties; it appears to be a higher polymerisation-product than the first."

This spontaneous polymerisation of 2,3-dimethylbutadiene to a rubber-like substance, observed by Kondakow, *is strikingly like the spontaneous polymerisation of isoprene to a rubber-like substance*, observed by Tilden. There also seems to be some reason for believing that this similarity in the behavior of the two hydrocarbons, and a possible relationship of their polymerisation-products, were discussed in Kondakow's original paper[2] of 1901. It has been stated that this paper was written in Russian, and the Editor of the *Journal fur praktische Chemie* cut out some of the theoretical speculations of Kondakow, hence, they did not get into the German or English literature. At all events, Kondakow[3] now claims that he, *and not the chemists of Bayer & Co.*, was the real discoverer of the first homologous rubber. Prof. Perkin, Jr. and some others seem to support Kondakow's claim, while Prof. Harries and Bayer & Co. do not acknowledge it.

It appears to me that one of the most important arguments in favor of Kondakow's claim is found in two articles written by C. O. Weber on December 5, 1902, and January 23, 1903, for the "Gummi-Zeitung." In his 1902 communication,[4] Weber says:

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[1] *J. prakt Chem*, **64**, 109, 110

[2] See review on Kondakow's book and claims to priority, by Dr. K. Gottlöb, *Gummi-Ztg*, **26**, 1546, 1582, 1628 (1912).

[3] Le caoutchouc synthènque, see homologues et ses analogues, *Rev. gèn. chim. pure et apphquèe*, **1912**, 129.

[4] *Gummi-Ztg.*, **1902**, 207

"In the *Journal für prakt. Chemie* for 1901, Bd. 64, page 109, J. Kondakow describes a most remarkable case of the polymerisation of 2,3-dimethyl-1,3-butadiene, which substance might be more concisely termed methylisoprene.

"To those who have carefully followed the evolution of the chemistry of rubber, it is well known that Bouchardat, Tilden and I have shown that isoprene may be reconverted or polymerized into rubber. Kondakow finds that his dimethylbutadiene, a liquid boiling at 69.5°, is spontaneously polymerised, on standing for 12 months, into a white, solid, spongy, elastic mass, whose physical properties resemble those of rubber. This polymerisation-product is distinguished from rubber, however, by the fact that it is insoluble in any of the known solvents for rubber. Therefore, this product, when considered from the chemical view-point, is undoubtedly to be regarded as the first known homologue of rubber, and it affords us the first concrete example of the possibilities which are scarcely suspected at the present day, and which will find their realization with the artificial production of rubber."

"It must be apparent to every manufacturer that such a rubber (as Kondakow describes) would have an enormous importance for the industry, since this rubber, even when not vulcanized, is totally unaffected by all solvents and oils, while in the vulcanized condition it would show no tendency to swell up in liquid hydrocarbons as benzene, petroleum, etc., and in oils."

In his 1903 article,[1] Weber repeats his statement that Kondakow's product is to be regarded as the *first known homologue of rubber.*"

In a paper written in 1912, E. Grandmougin[2] says: "The fact that not only isoprene, but also dimethylbutadiene may be polymerized to rubber-like substances, was recognized by Kondakow about the year 1900; and the importance of this observation, which furnished the possibility of producing homologous rubbers, was thoroughly appreciated at that time."

On the other hand, Friedr. Bayer & Co.,[3] of Elberfeld, in their patent of December 27, 1909, covering the method of preparing a rubber from 2,3-dimethylbutadiene, call attention to this work of Kondakow, and point out that his first product was soluble in alcohol while natural rubber is completely insoluble in alcohol; hence they conclude that Kondakow's first product was not an analogue or homologue of rubber, but was a lower polymerisation-product of the hydrocarbon. They also argue that the very insoluble second product of Kondakow is likewise no analogue of rubber, as indicated by its properties, but that it is probably a much higher polymerisation-product than natural rubber. They advise that in the process of making true 2,3-dimethylbutadiene rubber, the process must be carefully controlled by suitable tests so that the operation shall be continued until the resulting product reaches the condition of being insoluble in alcohol, but soluble in benzene.

It is also interesting to note that in "The India Rubber Journal" for February 8, 1913, page 10, is an article on the "Manufacture and Production of a Caoutchouc-like Substance." This article states:

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[1] *Gummi Ztg.*, 1903, 374

[2] *Ibid.*, 1912, 862.

[3] Deutsche Patentanmeldung, F.29010, Kl 39b, Gr. 1, vom 27 Dezember, 1909.

"The foreign correspondents of the patentee have found that the product obtained by Kondakow from β,γ-dimethylerythrene (β,γ-dimethylbutadiene) (*J. prakt. Chem.*, **64**, 109–110) can be converted by heating, preferably under pressure, into a technically valuable elastic caoutchouc-like product. For example, the Kondakow product is heated for eight hours in a closed iron vessel to from 150° to 200°. A compact, elastic mass is thus obtained. Patent No. 13,591."

Regarding this insoluble product obtained by Kondakow in 1901, Prof. Harries says:[1]

"I know this product very intimately, since I have had it in large quantities at my disposal. It does, in fact, have a certain connection with normal dimethylbutadiene rubber, but is in itself scarcely to be looked upon as rubber, for, after it stands in the air for a short time it changes into a peculiar, sticky, tough mass, readily soluble in the usual solvents, which is certainly useless for any technical purposes. Dimethylbutadiene rubber, obtained by heating dimethylbutadiene for a long time in a sealed tube at 90°–110°, acts entirely differently."

Again, Harries says:[1] "On splitting up normal dimethylbutadiene rubber, a practically quantitative yield of acetonylacetone is obtained, while Kondakow's insoluble, spontaneously polymerized product, and the soluble resin formed by allowing the latter to stand in the air, both yield at the most only 40 to 50% of acetonylacetone; it is also to be noted that the two latter products also yield an unknown aldehyde, boiling at about the same temperature as acetonylacetone.

"The decomposition curves of the diozonide of normal butadiene rubber, and the corresponding curves for the diozonides of the Kondakow products show great differences."

In reply to Prof. Harries' criticism of his support of Kondakow's claim to priority, E. Grandmougin[2] says:

"Although the investigations of Harries and of Bayer & Co. have shown that Kondakow's product is not a true rubber, but only yields a technically useful product through polymerization by heat, this does not change my views in the matter. The fact is, that as early as the year 1902 the possibility of preparing synthetic rubber from isoprene, and homologous rubbers from the butadienes was recognized, and the importance of this observation was at that time no secret to the specialists in this field. The technical development of the discovery, especially the manufacture of the raw materials in sufficient quantity, as well as the study of the polymerization processes, belong to the following period. Later investigators, as Harries, Hofmann, Coutelle, and others, deserve the credit of having shown the possibility of the technical accomplishment of the synthesis of rubber and analogous products."

However, until some better proof is offered, I believe we shall have to regard Kondakow's products as *not* being true dimethylbutadiene rubbers.

Prof. Perkin, Jr. cites the following references as observations made by various workers "on a variety of compounds, all of which are characterized by containing the conjugated double linking,

$$-\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}-.$$

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[1] *Ann.*, **395**, 215.

[2] *Chemiker-Ztg.*, **1913**, 502.

The polymerides obtained were mostly incompletely investigated, but their behaviour with solvents showed a general resemblance to that of rubber."

(1) The work of Harries[1] in 1901 on dihydrotoluene. Harries says: "The hydrocarbon (dihydrotoluene) resinifies readily, and on every distillation it leaves a small amount of a thick, yellow oil."

(2) The work of Klages in 1902 and 1904 on phenylbutadiene. In 1902, Klages[2] stated: "Phenylbutadiene boils at 94-96° under 18 mm. pressure; on distillation under ordinary pressure, it polymerizes to high boiling products. When exposed to the air, it resinifies forming a colorless balsam." In 1904, Klages[3] stated: "Phenylbutadiene is soluble in any proportion in ether, alcohol, and benzene, forming clear solutions; but it often changes after a few days and then gives opalescent solutions, which, after long standing, throw out white flakes. It gradually polymerises to a thick mass, which is insoluble in alcohol and ether, but is soluble in benzene."

(3) The work of Kronstein[4] in 1902 on cyclopentadiene. Kronstein gives the following: "The formation of dicyclopentadiene (from cyclopentadiene) requires several days at certain temperatures. It was to be expected that the formation of the dicyclopentadiene could be hastened by heating. For this purpose, I heated pure cyclopentadiene in a closed tube at 160°. After heating for five hours, the liquid commenced to become cloudy, and a white, solid substance separated in the form of a white powder. The separation of this solid continued as long as there was any unchanged cyclopentadiene present. The end-product is a slightly yellowish colored, opaque, solid substance."

"This solid substance may be completely reconverted into the monomolecular cyclopentadiene by the action of heat. The new polycyclopentadiene is insoluble in all solvents."

(4) The work of Willstätter and Veraguth[5] in 1905 on α-cyclooctadiene. These investigators state the following: "Cyclooctadiene may be purified by distillation over metallic sodium in vacuum; under 16.5 mm. pressure, it distills over as a clear, limpid oil and leaves little solid residue. It cannot be distilled under ordinary pressure, for as soon as it commences to boil the thermometer rises to 135 150°, and polymerization takes place very quickly and explosively with the formation of a gelatinous mass." "α-Cyclooctadiene shows an unusually strong tendency to polymerise. Even after standing for a short time, the liquid is converted into a solution of the dimolecular compound, which crystallizes out on strong cooling, but again dissolves at the room temperature. On standing for two to three days at the room temperature, the hydrocarbon is converted into a hard mass, which consists for the most part of the crystalline dicyclooctadiene; on the other hand, rapid polymerization at elevated temperatures converts about half of the hydrocarbon (1.8 grams out of 4 grams) into a higher molecular polymerisation-product."

"The dicyclooctadiene is very readily soluble in all organic solvents even in the cold. On standing in the air, it rapidly resinifies with absorption of oxygen."

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[1] *Ber.*, 34, 303.

[2] *Ibid.*, 35, 2650.

[3] *Ibid.*, 37, 2310.

[4] *Ibid.*, 35, 4151.

[5] *Ibid.*, 38, 1976, 1977, 1979, 1980, 1981.

"The higher molecular polymeride, formed at elevated temperature, forms a powder which does not melt up to 300°, and is extremely insoluble, crystallizing only from xylene. It remains unaltered in the air. It was not obtained pure enough to give good results on analysis, but it was shown to contain considerably more oxygen than dicyclooctadiene."

"This tendency towards polymerization exhibited by α-cyclooctadiene is of especial interest, owing to the recent important investigations of C. Harries, according to which there is indicated a connection between rubber and cyclooctadiene, and a cyclooctadiene appears to be the actual parent substance of para-rubber."

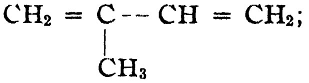
In 1907, Willstätter and Veraguth[1] described an isomeric cyclooctadiene, which they distinguished from the above described compound (α-cyclooctadiene) by the term β-cyclooctadiene. They stated: "The chief distinction between the two cyclooctadienes consists in the stability of the β-hydrocarbon; while α-cyclooctadiene polymerizes rapidly and often with an explosion, the β-compound suffers no change either by keeping for several months or by continued boiling."

(5) The work of Willstätter and Bruce,[2] in 1907, on bromobutadiene. They state: "Bromobutadiene is a readily mobile, very volatile liquid. On keeping, it is changed into a dark brown thick mass having little solubility; it is apparently a polymerisation-product."

The work of E. Knoevenagel,[3] in 1906, on 1,1-dimethylbutadiene should also be mentioned. He says: "When isoheptadienic acid is treated with dilute sulfuric acid, carbon dioxide is split off, and there results, possibly with the intermediate formation of a lactone—as the chief products, two hydrocarbons, C_6H_{10},

$$(CH_3)_2C = CH - CH = CH_2,$$

and a dimolecular substance, $C_{12}H_{20}$; this dimolecular compound is probably formed by the polymerization of the hydrocarbon, C_6H_{10}, in a manner similar to the formation of dipentene, $C_{10}H_{16}$, from isoprene, C_5H_8,



$$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH = CH_2;$$

accordingly, it would have to be regarded, like dipentene, as a cyclohexene derivative. Together with the two above mentioned hydrocarbons, a small amount of a higher boiling product was obtained, which, according to its boiling point, may be regarded as a trimolecular hydrocarbon, $C_{18}H_{30}$.

"The detailed description of the properties of these substances, and their relation to already known compounds will be given later in another place. Moreover, in view of the formula suggested by Harries for para-rubber, it is proposed to trace the possible connection which perhaps exists between the above mentioned hydrocarbons—more especially those having a straight chain of carbon atoms—and the rubber group; the connection may possibly be found in a different manner of polymerization."

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[1] *Ber.*, 40, 957, 964.

[2] *Ibid.*, 40, 3994.

[3] *Z. angew. Chem.*, [2] 19, 1330.

A careful review of the literature shows, therefore, that with the exception of Kondakow's leather-like, alcohol-soluble product and his higher molecular, insoluble polymeride obtained from 2,3-dimethylbutadiene, none of the earlier investigators described a rubber-like polymeride, or even anything approaching rubber-like, as resulting by the polymerization of an isomer or homologue of isoprene.

By some stretch of the imagination, we might possibly regard some of the solubilities of certain of these polymerides as resembling the solubilities of rubber, yet in all other important respects they were totally unlike rubber, *and by no means could they be termed isomeric or homologous rubbers.*

Prof. Perkin, Jr., sums up the position of synthetic rubber at the beginning of the year 1909 with these words:

"It was generally recognized that most compounds containing the conjugated double linking showed a tendency to polymerise, in some cases very readily, but in others with difficulty. The polymerides varied from sticky, indefinite substances, through well defined rubbers, to hard resins; their properties also varied somewhat with the method of polymerisation and with the molecular weight of the hydrocarbon polymerised. The methods of polymerisation included spontaneous polymerisation and polymerisation due to heat, sunlight, or the action of various chemical reagents, such as acids and alkalies. But, in most of these cases the methods in use were uncertain, wasteful or slow."

With one very important modification, I think we can all agree with this statement of Prof. Perkin, Jr. The part of his summary which I feel is *very* misleading, is his statement that "the polymerides varied from sticky, indefinite substances, *through well defined rubbers,* to hard resins." For, *with the exception of the work of Bouchardat, Tilden, Weber, and Wallach, on isoprene, and that of Kondakow on dimethylbutadiene,* there is, to the best of my knowledge, no reference in the literature by any investigator where "*a well defined rubber*" was ever formed as a polymeride from any conjugated double linkage compound, prior to the work of Prof. Harries and of Bayer & Co. in the year 1909.

HOBOKEN, N J

NEW BOOKS.

Les Progrès de la Chimie en 1912. Traduction Française autorisée des "Annual Reports on the Progress of Chemistry for 1912, Vol. IX," issued by the Chemical Society, London, Traducteurs, D. FLORENTIN, E GELIN, P. HUCHET, M. DRECQ, J. SAPHORES, P. POURQUERY. Paris Librairie Scientifique A. Hermann et Fils. 1913. Price, 7.50 francs

These well-known "Annual Reports" for 1912 contain the following divisions: General and physical chemistry, by G. Senter; inorganic chemistry, by E. C. C. Baly; organic chemistry, I, aliphatic series, by H. R. LeSueur, II, homocyclic series, by K. J. P. Orton, III, heterocyclic series and stereochemistry, by A. W. Stewart; analytical chemistry, by G. Cecil Jones; physiological chemistry, by W. D. Halliburton; agricultural chemistry and vegetable physiology, by A. D. Hall; mineralogical chemistry, by Arthur Hutchinson, and radioactivity, by Frederick Soddy.

It is gratifying to see the excellence and importance of these reports recognized by the publication of this translation. W. A. N

Logarithmic Reduction Tables. For Students in Analytical Chemistry. By CHARLES J. MOORE, Austin Teaching Fellow in Advanced Analytical Chemistry in Harvard University. Ginn and Co., Boston. 1913. 78 pp. Price, $1.00.

This little volume comprises 28 tables of data of especial interest to students of analytical chemistry, but of considerable interest to all chemical workers as well. The data have been collected from the most reliable sources, the authority being cited in all practicable cases. The selection of material is very good, including just about what the average worker will need in any ordinary calculation. Parallel with each value is its logarithm in six places, and those values which are often multiplied, as the atomic weights and the analytical factors, have logarithms of the multiples most used. Table 29 is a well-arranged table of six-place logarithms for general use. Following this come 14 pages devoted to very common sense explanations of the use of the tables and of logarithms. If this little book, with its attractive appearance and convenient arrangement, can stimulate students to a more habitual use of logarithms in chemical calculations, it will serve a very useful purpose in our colleges.

W. E. HENDERSON.

A Foundation Course in Chemistry. For Students of Agriculture and Technology. By J. W. DODSON, B. Sc (Lond), Lecturer in Chemistry at University College, Reading, and J. ALAN MURRAY, B Sc (Edin.), Lecturer in Agricultural Chemistry at University College, Reading Longmans, Green and Co , New York. 1913. x + 254 pp. Price, $1 10

This book presents a brief, pointed *description* of "those fundamental facts and general principles of chemistry upon which the superstructure of agricultural chemistry or other technical application must necessarily rest." Its scope and contents is shown by the following chapter headings: (1) Matter and energy; (2) air; (3) the chief gases of the atmosphere; (4) water; (5) hydrogen; (6) general principles; (7) oxides, acids, bases, and salts; (8) limestone; (9) common salt; (10) sulfur; (11) ashes; (12) sand, clay, etc.; (13) organic matter; (14) paraffins and their derivatives; (15) coal tar; (16) some common metals.

The materials mentioned in most of the headings are merely the starting points for the presentation of the chief elements contained in them, and for the common compounds made from them. Hence the chapter on *limestone* includes what in other texts is commonly included under the *oxides of carbon;* that on ashes, what is commonly included under *phosphorus;* etc. Seventy-five pages are devoted to organic chemistry, which appears to the reviewer to be a wise "innovation" in elementary text-books.

In the main, the selection of the topics shows discrimination and good judgment, and the presentation is brief, pointed, and clear. However, no attempt is made to point out the general relations or conditions which determine whether or no chemical changes will take place—not even the solubilities of acids, bases and salts are given or referred to in this connection. This is a serious defect. Otherwise the book is quite commendable, and should serve its purpose well. E. P. SCHOCH.

Cours Elémentaire de Chimie et de Minéralogie. Par DR. C I ISTRATI, Professeur de Chimie organique à l'Université de Bucarest, et DR. G G LONGINESCU, Professeur de Chimie inorganique à l'Université de Bucarest. Avec une Préface de CHARLES FRIEDEL, Membre de l'Institut Deuxieme édition française Publiée d'après la quatrième édition roumaine par A ADAM, Professeur agrégé au Lycée de Charlesville. Gauthier-Villars, Paris 1913 xii + 397 pp Price, 14 50 francs

This volume is designed by the authors primarily for use in secondary schools, and aims to present the subject inductively for beginners. Much stress is laid in the prefatory notes and introduction upon the fact that constant use is made of the atomic theory and the valence concept, which seems to be regarded as something of an innovation in works of this character. The opening chapter deals with water, as a familiar substance, and after a discussion of the general operations of solution, crystallization, distillation and filtration, the distinctions between physical and chemical changes are emphasized along customary lines. Chapters dealing with hydrogen, oxygen, the halogens, sulfur, and their compounds, follow in the order named, and at this point the atomic theory is introduced, and symbols, formulas and equations are first employed. The remaining chapters devoted to inorganic chemistry include the more common nonmetals and metals, closing with a brief presentation of the periodic law, the whole occupying two hundred and sixty pages. Of the remaining pages, one hundred and twenty are devoted to organic chemistry. The characteristic methods of preparation of the various types of organic compounds, and their behavior, including that of certain important representatives of each type, are given in considerable detail. The system of nomenclature used is that adopted by the International Commission at Geneva. The last few pages of the book are devoted to brief biographical notes regarding some of the more important workers in the chemical field. The entire text is freely interspersed with directions for experiments, which the pupil is expected to perform.

The book is notable for one feature, which the authors regard as most important, namely, extensive instruction in mineralogy, especially from its crystallographic side.

The course as presented in this book is not one which would be adaptable to our own secondary schools, nor would it probably meet the requirements of our college courses in its present form. The material is, however, thoughtfully presented, and, especially in the variety of experiments described, is of interest to teachers. H. P. TALBOT.

Elementary Chemical Theory. By J. M WADMORE. D. Van Nostrand Co., New York. 1912 xi + 275 pp. Price, $1.50.

In his preface the author says: "there is a growing tendency, and one much to be commended, to include more or less Chemical Theory in text-books of Inorganic Chemistry; Ostwald's 'Principles' is the prototype." "For school use the objection is that, though each point receives consideration as it crops up, and is well illustrated by concrete instances, the connection between different theoretical questions is obscured, and the elementary student, who is making his first acquaintance with the subject, fails to grasp it as a whole." The author also says he has been unable to find a suitable elementary book on Theoretical Chemistry; those now published "are too advanced, and too costly for school use." And again, his "book is not for those who, in a chemical sense, have grown their wisdom teeth, and with beginners, the obvious is just that which usually presents the most difficulty." With the last statement most teachers of chemistry will heartily agree.

There follow twenty-one short chapters with familiar titles such as: "Atomic Hypothesis;" "Vapor Densities;" "Periodic Law;" "Radioactivity;" "Constitution and Configuration of Compounds;" "Gas Laws and the Kinetic Hypothesis;" "Liquefaction of Gases;" "Solutions;" "Freezing and Boiling Points;" "Diffusion-Osmotic Pressure;" "Electrolysis-Ionization;" "Equilibrium of Electrolytes." Numerous interesting facts and comments, not often found in a work of this size, are included, so that but few could read the book through without learning something. Many of the topics are treated in a clear, concise way, wholly admirable. The chapter on the periodic law is particularly good.

The frequent use of historic allusions and apt quotations is an agreeable feature. The simplicity of language and expression in some chapters is almost excessive, but occasionally the author forgets the limitations of those for whom he is writing. For instance, the introduction of Baeyer's "strain hypothesis" and the giving, in degrees and minutes, the distortion of angles between the "carbon valencies" would seem to presume the existence of well grown "wisdom teeth." But these flights are few and short; a few pages further on may be found a painstaking explanation of the meaning of "inverse proportion."

In this country we are undoubtedly much under the dominion of German thought and methods—too much so some may think -and it is refreshing to read a book so frankly British. But a whole chapter (and one of the longer ones), dealing with osmotic pressure from the historic standpoint, in which van't Hoff's name is not even mentioned, is a curiosity.

The theory of electrolytic dissociation is approached with an infinitude of precautions, and is handled, metaphorically speaking, with tongs, like a hot crucible. On page 243 the student is solemnly admonished "that in its present form it is not accepted with quite universal consent." One cannot object to this warning, but it becomes rather amusing when compared with the direct and dogmatic way in which Callendar's osmotic hypothesis is presented in the previous chapter. This unevenness in selecting topics and in appraising theories is regrettable.

In the opinion of the reviewer, about two-thirds of the text is well adapted to the beginners for whom it is written, and the other third is interesting and suggestive reading for those much further advanced. So there is something for everybody in this book. S. LAWRENCE BIGELOW.

Theoretical and Physical Chemistry. By S. LAWRENCE BIGELOW, Ph D, Professor of General and Physical Chemistry in the University of Michigan xiii + 544 pp. The Century Company, New York 1912 Price, $3 00

This book was written for use in a course that should follow "the first courses in general chemistry and qualitative analysis" - as a text-book for sophomore or junior students. It aims to give the *advanced general* student in chemistry a large number of carefully selected and well discussed facts upon which the fundamental principles of the science are based. Such a book is greatly needed. The reviewer has examined this book repeatedly during a rather long period of time in which it has been before him, and he has recently also tried it as a text-book with just the class of students for which it is intended. It appears to him that the book fulfills its mission exactly, and that in its scope and general treatment of its subject matter it is excellent.

The scope of the subject matter is far greater than that of its famous prototype—Ostwald's *Grundriss der Allgemeinen Chemie.* We find among the headings not only all the familiar topics, but also the following: "Spectroscopic Evidences and the Theory of Inorganic Evolution;" "Luminiferous Ether and Vortex Rings;" "Radioactivity and the Electron Theory;" "Colloidal Solutions." Under many of the familiar topics are found new subheadings; thus, under "Osmotic Pressure" are found: "Attempts to Explain Osmosis, the Kinetic Hypothesis, the Attraction Hypothesis, the Surface Tension Hypothesis the Function of the Membrane-Capillary Structure-Membranes as Solvents, etc." Under "The Periodic System" we find mention of Loew and Erdman's *Archimedes Spiral Arrangement,* and of Crooke's *Genesis of the Elements.* These topics serve to increase the student's interest in the subject and widen his view of natural phenomena.

The book is very readable: the style is simple, direct, and very sympathetic to elementary students, hence they read the comparatively large number of pages readily and note the important points without effort.

Naturally, a book as large as this, and which deals with so many different topics is not without flaws and objectionable parts. However, they do not affect the book seriously as a whole, and since the first edition of the book is practically exhausted and the author is at work on a revised edition in which most of these slips and shortcomings will probably be corrected, none of them need be pointed out here.

The publishers have done their work well: the book is printed in clear type, on good paper, and is well bound. E. P. SCHOCH.

Experiments Arranged for Students in General Chemistry. (Shorter course) By EDGAR F. SMITH, Blanchard Professor of Chemistry in the University of Pennsylvania, and HARRY F. KELLER, Professor of Chemistry in the Central High School of Philadelphia. P. Blakiston's Son and Co, Philadelphia. 1913. vii + 56 pp. 12.5 × 18.5 cm. Price, $0.60, net.

This little volume contains, in condensed form, a well selected list of experiments taken from the larger volume by the same authors. It is primarily for high school use but may equally be adapted to short college courses. Though much too brief upon such important subjects as the oxygen compounds of sulphur and nitrogen, with their corresponding acids, it is to be remembered that these experiments have been selected mainly for the purpose of covering the entire field in as short a time as possible; to this end the authors have succeeded in presenting a selection clearly illustrative of the principles of general chemistry.

WILLIAM J. HALE.

Traité de Chimie Minérale. Par H. ERDMANN. Tome second. 8vo., 331 pp. A Hermann et Fils, Paris. 1914. Prix, 10 fr.

The first volume of this translation by Professor A. Corvisy of the fifth edition of the German work was noticed in the July, 1913, number of THIS JOURNAL.

The present volume deals with the metals exclusively. Extensive and interesting information is given in regard to their mineralogical origin, uses, compounds, statistics, history, etc. Like the preceding volume, it is a useful book for French-reading lecturers and students. It is hardly extensive enough to be used as a book of reference to compounds, except the more common ones. Some peculiarities of treatment have been noticed, which are doubtless due to the author's varying interest in the different metals. For instance, five and one-half pages are devoted to rubidium, while the more interesting, because extreme, metal caesium receives but little more than half a page of comment. The comparative rarity of caesium is hardly a good excuse for this brevity of treatment, for its compounds have been studied more thoroughly, probably, than those of rubidium. H. L. WELLS.

Traité de Metallographie. Par FÉLIX ROBIN. Préface de M. F. OSMOND. Libraire Scientifique A. Hermann et Fils, Paris. 1912. 464 pp. Price, 30.00 fr.

The book is an attempt to condense in one volume much of the more recent work on metallography. The author first discusses the general principles of metallography, the preparation of specimens, etching methods, etc., and follows with a description ,of the ideal alloy diagrams. This part of the subject is not adequately treated. He next deals with micro-chemical analysis and its application to the study of pure metals and alloys. The nature and microscopical appearance of the pure metals and the chief constituents of the common alloys are then considered. Special attention is given to the micrographic constituents of iron and steel and the descriptions are detailed and accurate. This is followed by outline descriptions of a large number of binary alloys with accompanying diagrams and photographs. Some of the equilibrium diagrams are taken from the earlier French alloy literature and are quite out of date. Most of the diagrams are satisfactory, however, and the microphotographs are excellent. In later chapters the author deals with the practical problems of steel metallography, such as the effects of mechanical treatment on structure, the effects of slag inclosures, etc. The final chapter deals with the microstructure of slags and similar metallurgical products.

The book contains a large amount of material not readily available, and, though some of the material does not seem to be very closely connected with metallography, much of it is distinctly useful. Special emphasis is laid on the microstructure and properties of steel, so that the book should be chiefly useful to the steel metallographist. It is profusely illustrated with 250 diagrams and 500 microphotographs, most of which are excellent and well reproduced. ROBERT S. WILLIAMS.

Treatise on General and Industrial Organic Chemistry. By DR ETTORE MOLINARI, Professor of Industrial Chemistry to the Society for the Encouragement of Arts and Manufactures and Merceology at the Luigi Bocconi Commercial University, Milan. Translated from the second enlarged and revised Italian Edition by THOMAS H POPE, B.Sc., A.C.G.I., F I.C., School of Malting and Brewing, University of Birmingham. P. Blakiston's Son & Co., Philadelphia xix + 770 pp. 10 × 6⅞. Price, $6.00.

The fact that a new edition of this book has been called for in only two years after the appearance of the first, and also that it is translated into both English and German, is evidence that it meets a real need. It presents a combination of theoretical with applied chemistry, though it has evidently not been the intention of the author to prepare a complete treatise on technological chemistry. Details are given only in the cases of some of the principal industries and especially in those well adapted to give a general idea of the different applications of chemical processes. For example, the industries of illuminating gas, sugar, beer, alcohol, acetic acid, dyeing, textile fibers, fats and soaps, explosives, etc., are dealt with, in more or less detail. Statistics of production, exportation and importation have been brought up to the year 1910 and in some instances up to

1911. Mr. Pope has made a number of alterations and additions, principally in amplifications of the statistics referring to Great Britain and the United States. M. V. DOVER.

Aus dem Kaiser Wilhelm-Institut für Chemie. Untersuchungen über Chlorophyll. Methoden und Ergebnisse. Von RICHARD WILLSTÄTTER UND ARTHUR STOLL. Mit 16 Textfiguren und 11 Tafeln. Verlag von Julius Springer, Berlin. 1913. $9^1/_2 \times 6^1/_2$. Paper. iv + 424 pp. Price, 18 marks.

In the preface, Professor Willstätter states that this book contains the unpublished investigations which he has carried on together with Mr. Arthur Stoll during recent years. These comprise the isolation of chlorophyll, the separation and quantitative estimation of all components of the coloring matter of the leaf, and the hydrolysis of chlorophyll.

In these investigations new methods for the preparation of chlorophyll and its decomposition products have been worked out. With the new experience thus gained and the more easily accessible materials, the earlier experiments on the transformations of chlorophyll have been repeated and most of the older processes improved.

In order to make this work a more complete representation of our knowledge of chlorophyll, it is supplemented with the results of the investigations which Professor Willstätter and his co-workers have published in *Liebig's Annalen der Chemie* during the last seven years. To these have been added some unpublished investigations on the pigments of the brown algae made by Professor Willstätter and Mr. H. J. Page and also those on the relation between chlorophyll and haemin, carried on with Mr. M. Fischer. Chlorophyll and haemin have been broken down to a common mother-substance with the aid of reactions, which throw some light on the essential differences in the constitution of chlorophyll and haemin.

Some idea of the book may be obtained from the following condensed table of contents: I. Theoretical Introduction; II. Description of the Coloring Matter of the Leaf; III. The Extraction of the Coloring Matters; IV. Quantitative Analysis of the Four Coloring Matters of the Chloroplasts; V. Isolation of Chlorophyll; VI. Isolation of the Two Components of Chlorophyll; VII. The Action of Chlorophyllase; VIII. Use of the Enzyme for the Partial Synthesis of Chlorophyll; IX. The Chlorophyllides; X. Isolation of the Components, *a* and *b*, of the Chlorophyllides; XI. Description of the Chlorophyllides; XII. The Yellow Pigments of the Chloroplasts; XIII. Phaeophytin; XIV. Method of Separating and Estimating Chlorophyll Derivatives; XV. The Phaeophorbides *a* and *b;* XVI. Phytochlorins and Phytorhodins; XVII. Phytol; XVIII. The Chlorophyllin Salts; XIX. Introduction of Magnesium into Derivatives of Chlorophyll; XX. Decomposition of Chlorophyll by Alkalies: Phyllins and Porphyrins; XXI. Oxidation of the Chlorophyll Derivatives; XXII. Reduction of the Chlorophyll Derivatives; XXIII. Etiophyllin and Etioporphyrin; XXIV. Decomposition Products of Haemin; XXV. Graphical Representation of the Absorption Spectra. The book also contains eleven plates of photographs of spectra and crystals.

It is hardly necessary to state that the book is a most excellent one and one of the most important contributions to our knowledge of chlorophyll that has appeared. As Professor Willstätter states in the preface, it makes chlorophyll and its derivatives easily accessible and will much facilitate investigation in this field by both chemists and physiologists.

W. R. ORNDORFF.

The Synthetic Dyestuffs and Intermediate Products. (Second Edition.) By JOHN CANNELL CAIN AND JOCELYN FIELD THORP. 8vo., 423 pp. C. Griffin and Co., Ltd., London. 1913. Price, 16 shillings, net

The first edition of this book, which appeared in 1905, was well received by all laboratory workers in color chemistry, and especially by teachers of the chemistry of the coal tar dyes, as it filled a placed in their libraries, which until then had been vacant.

In the second edition of this book the text has been revised where the authors considered it advisable, and owing to the advances which have been made in the synthesis and development of the so-called "vat colors," they have renamed two chapters of the book. The chapter formerly called "Oxyketone Dyestuffs" has been changed to "Anthracene Dyestuffs" so as to include indanthrene and related colors, and the chapter formerly entitled "Indigo" has been changed to "Indigoid Coloring Matters" and includes the many indigo derivatives which have been introduced during recent years. The authors have also thought it advisable to replace the tables of reactions on the fiber, published in the first edition, by the excellent tables recently elaborated by Green and his co-workers. The main features of the book are as follows:

Part I gives the theoretical description of the dyestuffs and their intermediate products, especial attention being paid to the orientation of the various groups as they enter the intermediate products, and their structural position in the dyestuff molecule. The discussion of the dyestuffs is arranged in accordance with a very complete structural classification and the comprehensive character of numerous complex structural formulas as well as their excellent typography, is worthy of special note.

Part II is devoted to the practical side of the subject and gives the working detail for the laboratory preparation of one or more typical members of each group of intermediate products and dyestuffs.

Part III is analytical in character and describes the processes actually in use in chemical and color works for the identification and analysis of intermediate products and dyestuffs. It includes tables for the identification of dyes on both animal and vegetable fibers, and an appendix of useful specific gravities tables.

This revised edition will be received with interest by all teachers of the organic chemistry of the dyestuffs, to whom the first edition has proved almost indispensable, and its use may well be extended to every laboratory worker and student of the subject. L. A. OLNEY.

Elements of Water Bacteriology. By S. C. PRESCOTT AND C. E. A. WINSLOW. Third edition. John Wiley & Sons, New York, 1913. Price, $1.75.

This excellent book, which first appeared in 1904, has now reached its third edition. Much new material has been inserted throughout the book and a new chapter has been added upon the "Bacteriological Examination of Shellfish." The recent recommendations of the Committee on Standard Methods are fully discussed, but the authors do not agree with the recommendation of the Committee that the 37° count should replace the 20° count. Their position is in fact that held by most practical workers in the field of water bacteriology. The authors also express their full sympathy with the view that the whole group of lactose-fermenting bacilli is significant in sanitary water analysis and that too narrow an interpretation of identification tests for *B. coli* is unwarranted. On this point, again, the opinion of Prescott and Winslow is probably shared by most American workers.

Little criticism can be made of details. It is possibly not quite fair (page 52) to discuss Miquel's numerical standards in comparison with others without reference to the special methods employed by that worker. On page 59, "warnings of danger" as to the character of a water supply based on "daily bacteriological analyses" are referred to with approval. The authors apparently overlook the fact that in surface waters of fluctuating character like some of those referred to, the "warnings" may not be given until long after the danger has passed, and conversely, that an assurance of safety may be made at a time when the water, perhaps in only a few hours, has changed for the worse.

The book as a whole is wonderfully well up with the times and is written with much spirit and discrimination. The material presented is for the most part thoroughly digested, and represents the best discussion of the sanitary bacterial examination of water to be found anywhere.

EDWIN O. JORDAN.

VOL. XXXVI. FEBRUARY, 1914. NO. 2.

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THE ELECTRON CONCEPTION OF VALENCE. V. POLAR AND NON-POLAR VALENCE.

BY K. GEORGE FALK AND J. M. NELSON

Received January 1, 1914

The dualistic view of the nature of valence was considered at some length in a paper by Bray and Branch entitled "Valence and Tautomerism" which appeared recently in THIS JOURNAL.[1] That is to say, the union between two atoms in a molecule was taken to be "either polar or non-polar in character, according as it is assumed that an electron passes completely or does not pass from one atom to the other," a view that is not entirely new.[2] The present writers have been interested for some years in questions of this nature and have published a series of papers[3] in which were presented the conclusions drawn when valence is considered to be polar in character only. The views of Bray and Branch with regard to the two kinds of valence are somewhat at variance with this point of view.

It is desirable, in the first place, to compare the nomenclature of Bray and Branch with that used in the IV Paper of this series in which a "Classification of Chemical Reactions" was developed. Their "polar number" corresponds to the algebraic sum of the charges carried by an atom as stated in the IV Paper, and their "total valence number" to the arithmetical sum of these charges.

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[1] 35, 1440 (1913).

[2] The nature of valence as dualistic in character was taken up by Nernst in the different editions of his "Theoretische Chemie," for instance, in the IV edition (1903), p. 400; VII edition (1913), p. 435.

[3] S. of M. Quarterly, 30, 179 (1909). THIS JOURNAL, 32, 1637 (1910); 33, 1140 (1911); 35, 1810 (1913). *Orig. Communications VIII Intern. Congr. Applied Chemistry,* 6, 212 (1912); *J. prakt. Chem.* (*N. F.*), 88, 97 (1913).

In the second place the important fact must be mentioned that the non-polar valence view in itself is now generally recognized not to be a sufficiently broad basis upon which to classify valence phenomena. Either the dualistic view of polar and non-polar bonds, or the unitary view of polar bonds alone appears to be essential for a satisfactory classification.

Bray and Branch assume that polar and non-polar bonds differ fundamentally in kind. The consideration of oxidation and reduction leads to some anomalous relations when taken up from this point of view. The correct definition for these phenomena with inorganic compounds is unquestionably that involving a change in the electrical charges of the atoms taking part in the reaction,[1] gain of positive charges by the reacting atoms for oxidation, loss of positive charges for reduction. For compounds with non-polar valences it is difficult to formulate a definition. A description of the different oxidation or reduction reactions of organic compounds on the dualistic valence view leads to contradictions. The organic reactions in which a hydrogen atom attached to carbon is replaced by a halogen atom and the halogen atom by a hydroxyl group, may be taken up briefly. When chlorine, combined with carbon is replaced by a hydroxyl group, the experimental evidence, mainly that derived from hydrolysis experiments,[2] points to the same kind of valence for the chlorine and oxygen atoms when these are combined with carbon. If this is admitted, then the replacement of hydrogen by halogen will be an oxidation reaction, and in general, the definition of oxidation might then be stated as "an increase in the proportion of its oxygen or acid-forming element (or group)" and of reduction as "subtracting oxygen or an acid-forming element (or group)."[3] This is however a re-statement in a somewhat different form of the definition of oxidation and reduction in which electric charges are involved as was shown in the IV Paper. The dualistic view, on the other hand, assumes the hydrogen atoms and the chlorine atoms to be combined with the carbon atom by non-polar valences. If it is not admitted that the chlorine-carbon linking is polar, it would be necessary, since experimental evidence shows no change in charges when halogen is replaced by hydroxyl in these compounds, for the bond between carbon and oxygen (of hydroxyl) to be non-polar in character. If this is done, then the phenomenon of oxidation in organic compounds would possess an entirely different significance from that which it does in inorganic reactions. On the non-polar view, chlorination consists of a simple replacement of hydrogen by chlorine, oxidation would then consist of a simple replacement of hydrogen by hydroxyl (or oxygen), and the series of transformations methane ⟶ methyl alcohol ⟶ formaldehyde ⟶ formic acid ⟶ carbon dioxide, for example, would represent replacements with no change in the charge of the carbon. Such a view is evidently untenable, if only because of the artificial differentiation between reactions, some of which, for convenience of treatment, are classed with organic compounds, others with inorganic compounds, which it introduces, and the absolutely separate characterization of reactions involving oxidation for organic and inorganic substances as distinct and unrelated phenomena.

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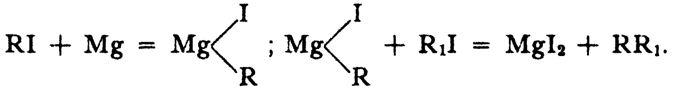
[1] Practically every modern text-book of inorganic or analytical chemistry, which takes up these relations uses the change in electrical charges as the principle underlying the phenomena of oxidation and reduction. The treatment given by Stieglitz in his "Qualitative Analysis," Vol. I, Chapter 14, is particularly clear and instructive.

[2] Cf. IV paper of this series, p. 1816, as well as the work of Stieglitz, Selivanow, W. A. Noyes, and others there referred to.

[3] Cf. Treadwell-Hall, "Qualitative Analysis" (1911), p. 3, and other text-books.

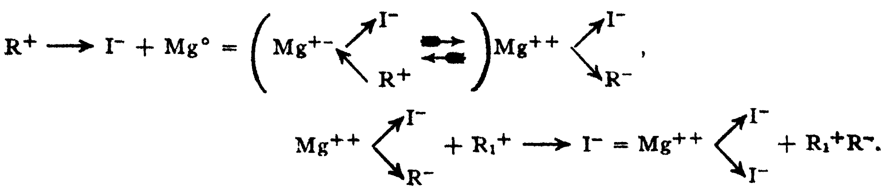
It is also of interest to study some specific substance or reaction in order to determine whether the dualistic polar and non-polar valence view, or the unitary polar valence view will supply the more satisfactory classification. In the simple hydrocarbons and their halogen derivatives, the dualistic view assumes non-polar valences.[1] The transformations which these substances undergo in the Grignard reaction, may therefore be chosen as a test. Here the reaction may be formulated in the most general form as follows:



$$RI + Mg = Mg\left\langle\begin{matrix}I\\R\end{matrix}\right. ;\ Mg\left\langle\begin{matrix}I\\R\end{matrix}\right. + R_1I = MgI_2 + RR_1.$$

In this reaction, omitting the action of the solvent or other catalytic agent, the change consists of RI and R_1I, both with non-polar valences on the dualistic view, reacting with the element magnesium to form non-polar, RR_1 and magnesium iodide. The latter substance must surely be assigned polar valences.[2] It is, therefore, necessary to assume a change at some stage in the character of some of the valences in the reactions, but no indication is apparent when this change is to be assumed. That the magnesium iodide may act as an electrolyte surely cannot be taken as an indication when this change takes place, since this is an effect and not the cause.

Take, on the other hand, the polar view of valence in this reaction; then the following formulation may be given:



$$R^+ \longrightarrow I^- + Mg^\circ = \left(Mg^{+-}\left\langle\begin{matrix}I^-\\R^+\end{matrix}\right. \rightleftarrows \right)Mg^{++}\left\langle\begin{matrix}I^-\\R^-\end{matrix}\right. ,$$

$$Mg^{++}\left\langle\begin{matrix}I^-\\R^-\end{matrix}\right. + R_1^+ \longrightarrow I^- = Mg^{++}\left\langle\begin{matrix}I^-\\I^-\end{matrix}\right. + R_1^+R^-.$$

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[1] Bray and Branch, *Loc. cit.*, p. 1443.

[2] *Ibid.*, p. 1442.

The first action consists of the combination of R^+I^- and atomic uncharged magnesium. The latter is indicated by the symbol Mg° in order to bring out more clearly the change which it undergoes in the course of the reaction. The possible intermediate product $Mg^{+-}\!\begin{array}{l}\nearrow I^- \\ \nwarrow R^+\end{array}$, is given in the equation for the sake of completeness and to make the electrical character of the change involved clearer, but no stress is laid on the formulation of this hypothetical substance. The first definite product formed is represented by $Mg^{++}\!\begin{array}{l}\nearrow I^{-\,1} \\ \searrow R^-\end{array}$. The formation of this compound involves a change in the electrical character or valence of the magnesium and of one of the atoms of group R. As represented in the equation, the magnesium is oxidized, its valence changing from 0 to +2, and a carbon atom of the group R reduced two units of valence. The next reaction is a simple metathesis with the formation of magnesium iodide and $R_1^+R^-$. With the polar view of valence, no assumption as to a change in the nature of the valences is necessary, and it seems much simpler and more satisfactory to follow the transformations from this point of view than with the combination of the two kinds of valence, polar and non-polar.

Other examples of the Grignard reaction might be cited to illustrate the arbitrary nature of the changes which it would be necessary to assume in the character of the valences of the atoms undergoing change if the dualistic valence view be adopted. Other reactions also show this, the Würtz synthesis being a particularly instructive type of reaction. The reaction here may be written

$$2RI + 2Na = RR + 2NaI.$$

On the dualistic view, the sodium iodide contains polar valences, the

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[1] The reasons for giving the bonds the directions indicated, or for considering the electrical charges distributed as shown, have been given in some detail in the previous papers of this series. Briefly summarized, the principles employed are based upon the arrangement of the elements in the periodic system, in the horizontal groups the elements of smaller atomic weight tending to give up corpuscles in forming chemical bonds to the elements of higher atomic weight, while in the vertical groups, those of higher atomic weight give up corpuscles (are more positive) to those of lower atomic weight. These rules may only be looked upon as general guiding principles, in particular the main and sub-groups of the vertical series must be treated separately. The phenomenon of ionization in solution with those compounds for which it has been observed, furnishes an invaluable experimental method for determining the distribution of the electric charges. Caution must be exercised, especially with organic compounds where isomeric substances exist in which the isomerism may be taken to depend upon different directions of the valences. The general principles outlined apply to the more stable linkings between atoms, while the less stable linkings may be present in isomeric substances showing less stability. This question has been discussed more fully in the previous papers.

RI and RR non-polar valences. Here also, as in the Grignard reaction, the question as to when the iodine changes its valence from the non-polar to the polar kind remains unanswered. On the polar view of valence, the reaction is formulated

$$2R^+ I^- + 2Na^\circ = R^+ R^- + 2Na^+I^-.$$

The change is seen to consist of the oxidation of the sodium, its valence changing from 0 to +1, and the reduction by two units of valence of one of the carbon atoms of one of the two molecules of reacting RI. The character of the iodine remains unchanged. The sodium in this reaction (as also the magnesium in the Grignard reaction) plays an analogous part to its behavior in purely inorganic reactions in which it is oxidized from the metallic state, at the same time causing a reduction of one or more atoms in some other substance. The only difference lies in the fact that these oxidation and reduction changes are not as apparent and as easily followed with carbon compounds as with some inorganic compounds. Fundamentally, however, there is no reason to assume a difference. Similar relations hold true for other organic reactions. In fact, in the experience of the writers, every organic reaction can be interpreted simply and satisfactorily and brought into relationship with the reactions of inorganic chemistry by using polar valences, while the use of the dualistic view involving polar and non-polar valences introduces arbitrary and unnecessary complications in following the chemical reactions. Other reactions will not be considered here, but will be presented in extended form in another connection.

A possible way out of the difficulties involved in the dualistic view is contained in the paper by Bray and Branch and also in a paper by Lewis.[1] They assume the same compound or grouping to contain at one time polar valences and at another time non-polar valences. No direct evidence can, of course, be presented against such a view, and it might serve a useful purpose if it were possible to determine the conditions of such hypothetical changes, but until this has been done, it appears to add only a further arbitrary complication to the consideration of valence structures. Ionization in solution is of the greatest value in determining the distribution of electric charges in substances which ionize, but, on the other hand, the absence of ionization must not be taken as evidence regarding the presence or absence of polar valences. The phenomenon of ionization depends to a great extent on the nature of the solvent[2] and there is no evidence which leads us to suppose that the presence or absence of the property of ionization of substances depends altogether on the presence of polar or non-polar valences in them or on the nature of the linking between the atoms as presumed in the dualistic view.

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[1] THIS JOURNAL, 35, 1449 (1913).

[2] Cf. Walden, THIS JOURNAL, 35, 1649 (1913).

It will be seen, therefore, that the dualistic view of valence introduces complications in the theoretical treatment of chemical reactions which may be avoided to a great extent if the unitary polar valence view be adopted throughout. The positive results which have been obtained with the unitary view must also be emphasized. The work of Stieglitz[1] must be mentioned especially in this connection. Not the least important feature of this view is the possibility of grouping together all chemical phenomena. The IV Paper of this series dealt especially with this point of view and the Classification of Chemical Reactions developed there shows how the principles may be applied to organic as well as to inorganic reactions.

Finally, therefore, the relations pointed out in this paper and a number of other facts, some of which have been mentioned in the previous papers, have convinced the writers that the polar view of valence (or the valence view which considers chemical bonds to be formed by the transfer of corpuscles between atoms) is sufficiently broad to enable a satisfactory classification of valence phenomena to be developed at present, and it is this fact which it is desired to emphasize in this paper in contradistinction to the classification of Bray and Branch which involves both polar and non-polar valences. Especially in oxidation and reduction reactions with organic as well as with inorganic compounds does the unitary view, in which the changes are assumed to depend upon the electrical charges of the atoms, show a simpler and more satisfactory classification than does the dualistic view which leads to contradictions or to an arbitrary separation of phenomena fundamentally similar.

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The Nature of the Forces Holding Atoms in Combination.—The magnitude of electrical forces in comparison with that of gravitation, which seems to be the other force most worthy of consideration, makes it seem quite improbable that the atoms of such compounds as hydrochloric acid, hydriodic acid and water are held together by electrical forces while those of methane and ethane are held by gravitation or some other non-electrical force. From the experiments of E. C. Franklin, especially, it seems quite clear that we have positive hydrogen and negative amide, NH_2, in ammonia, just as we have positive hydrogen and negative hydroxyl in water. There is considerable evidence that acetylene, $H—C\equiv C—H$, contains positive hydrogen but, if this is true, it is hard to believe that ethane, $H_3C—CH_3$, from which it can be obtained by simple reactions, does not also contain positive hydrogen. W. A. NOYES.

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[1] Stieglitz and Curme, *Ber.*, 46, 911 (1913). Curme, THIS JOURNAL, 35, 1143 (1913). Cf. also W. A. Noyes, THIS JOURNAL, 35, 767 (1913) and the references to the work of others along similar lines given there.

NEW CRYSTALLINE SILICATES OF POTASSIUM AND SODIUM, THEIR PREPARATION AND GENERAL PROPERTIES.

By George W. Morey.

Received January 5, 1914.

Of the large and complex group of silicates, those of the alkalies are presumably the easiest to study experimentally, and yet our present knowledge of them is fragmentary. An investigation was accordingly undertaken with the idea of obtaining more definite knowledge of the properties of these compounds, as it is evident that from a study of them it should be possible to obtain information of value in attacking the larger problems relating to the complicated natural silicates. It is the purpose of the present paper to describe methods and apparatus used in the preparation of some new silicates of potassium and sodium, and to point out some of their general properties; their physico-chemical relationships, the investigation of which is now well under way, will be taken up in a later paper.

Historical.

In discussing the present status of our knowledge of the alkali silicates, it seems unnecessary, in view of the recent excellent summary by Jacoby,[1] to take up the rather voluminous literature of the subject *in extenso*. Moreover, we shall consider in this paper only work carried out in the wet way; first, because the new experimental work here recorded deals entirely with the system alkali silicate and water, and secondly, because the other side of the subject has already been discussed by Niggli[2] in his paper on the system alkali carbonate and silica.

Up to the present time, no well-defined crystalline silicate of either potassium or sodium has been prepared in the wet way. It is true that several authors have described crystals of hydrated sodium metasilicate obtained from aqueous solution at ordinary temperature, but the observations recorded are not thoroughly concordant. Thus Petersen[3] describes a monoclinic substance containing 5 molecules of water; Fritsche[4] describes in detail triclinic crystals containing 6 aq., and also a compound containing 9 aq.; York[5] reports 7 aq.; several observers have reported 8 aq., including von Ammon,[6] who describes the monoclinic crystals which he obtained; Jordis[7] found 6–12 aq.; and Vesterberg[8] found 9 aq. and, from dehydration experiments, concluded that hydrates containing 3 aq. and 6 aq. also exist. Furthermore, both Jordis and Vesterberg made experiments with sodium silicate solutions containing a great excess of alkali—in one case 14 Na_2O to 1 SiO_2—but they obtained no crystals richer in alkali than the metasilicate.

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[1] Gmelin-Kraut, "Handbuch der anorganischen Chemie," 7 Auflage, Bd. III, Abt. I, pp. 222–3 and 229–34 (1909).

[2] P. Niggli, This Journal, **35**, 1693–1727.

[3] Petersen, *Ber.*, **5**, 409–11.

[4] Fritsche, *Pogg. Ann.*, **43**, 135 (1838).

[5] York, *Trans. Roy Soc. London*, **1857**, 533–42.

[6] von Ammon, *Inaug. Diss., Göttingen*, **1862**.

[7] Jordis, *Z. anorg. Chem.*, **56**, 305 (1907).

[8] Vesterberg, *Orig. Comm. VIII Intern. Congr. Appl. Chem.*, **2**, 235–9.

From this there seems to be no doubt that Na_2SiO_3 forms several crystalline hydrates; none of these, however, have been encountered in the work described in this paper. The question of the composition and range of stability of each of the possible hydrates is still an open one, and can be answered only by an investigation undertaken with this specific purpose in view.

Aqueous Solutions.—The alkali metasilicates, as ordinarily prepared, are largely hydrolyzed,[1] the silica separating in colloidal form.[2] It must be emphasized, however, that conclusions in regard to the relative strength of silicic acid, based on the apparent degree of hydrolysis of such solutions, are not necessarily valid; indeed, there is ground for the belief that silicic acid is considerably stronger than has generally been supposed, just as is the case with aluminic acid.[3] In any case, solubility experiments, such as those made by Vesterberg,[4] are meaningless, because the phenomenon is one of decomposition. When, for instance, hydrated sodium metasilicate is treated with water, the first infinitesimal portion dissolved is immediately decomposed with the formation of colloidal silica, and the process will go on until some more or less definite end point is attained; but this presumed equilibrium is in no way determined by the real solubility of the sodium silicate itself.

A number of investigators have obtained products containing from two to four, or more, molecules SiO_2 to one molecule alkali oxide, but the preparative methods used are, in every case, open to question, and the products were, without exception, amorphous. Most of the methods fall into two classes: (1) precipitation with alcohol, and (2) determination of the ratio alkali oxide: silica in the saturated solution. The first method, by which, *e. g.*, Forchhammer[5] obtained products of the gross composition $K_2O.2SiO_2$, $K_2O.8SiO_2$, and $Na_2O.3SiO_2$, was shown by Ordway[6] to lead to wholly erroneous conclusions, because the composition of the precipitate depends on the concentration of the solution, the proportion of alkali present, and the amount of alcohol added, and varies continually with variation of any of the above factors. That the second method should lead to equally unreliable conclusions is obvious, so that the wide discrepancies between the results of various observers are to be expected. Kohlrausch,[1] however, from conductivity determinations, concluded that $Na_2O.2SiO_2$ was the richest in SiO_2 of any compound of Na_2O and SiO_2 existing in aqueous solution, and that solutions of the metasilicate contain NaOH and $Na_2Si_2O_5$.

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[1] Loomis, *Wied. Ann.*, **60**, 533 (1897); Kahlenberg and Lincoln, *J. Phys. Chem.*, **2**, 77 (1898); Kohlrausch, *Wied. Ann.*, **47**, 756–64 (1893); *Z. physik. Chem.*, **12**, 773 (1893).

[2] Jordis, *Z. anorg. Chem.*, **56**, 297 (1907); Mylius, *Atti. VI Congr. Intern. Appl. Chem.*, **1**, 682 (1907); Kahlenberg and Lincoln, *loc. cit.*; Kohlrausch, *Loc. cit.*

[3] Blum, THIS JOURNAL, **35**, 1499–1505 (1913).

[4] Vesterberg, *loc. cit.*

[5] Forchhammer, *Pogg. Ann.*, **35**, 343 (1835).

[6] Ordway, *Am. J. Sci.*, [2] **33**, 27–36 (1862).

To sum up then: our knowledge of the silicates of sodium and potassium up to the present time has been limited to the facts that these silicates, as they have ordinarily been prepared, dissolve in water, forming solutions which are largely hydrolyzed, and in which most of the silica exists in colloidal condition; and that sodium metasilicate forms one or more crystalline hydrates.

Experimental.

The experimental work was carried out by the so-called hydrothermal method, the substances being treated in closed bombs with water at high temperatures, and at the consequent high pressures. The apparatus used has been completely satisfactory; its construction is simple, it is easy to manipulate, and it secures absolute freedom from leak—over 200 experiments have been made without a single leak—a condition which, combined with the reliability of the temperature determinations, insures the reproducibility[2] of the results.

Construction of the Bombs.—The construction of the bombs is shown in Fig. 1, which is drawn to scale. Each bomb consists essentially of three parts, namely, the body *E*, the plunger *C*, and the screw plug *B*, all made from tool steel.[3] The body is made from a cylinder 3 inches in diameter and 8 inches long, by boring out a $1^1/_4$ inch hole to form the chamber;

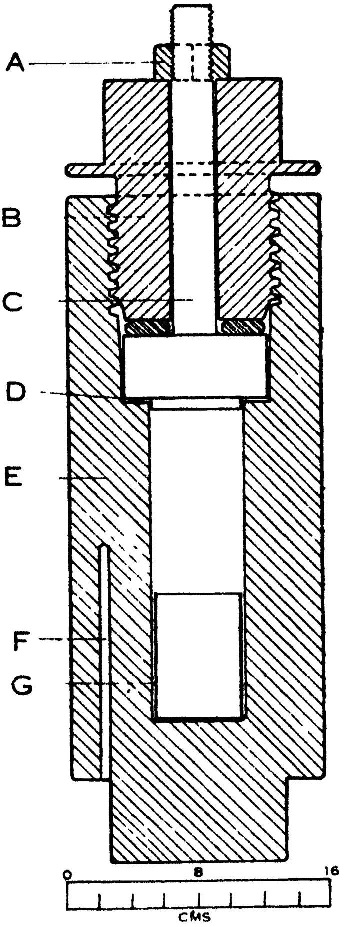

Fig. 1.—Diagram showing the construction of the bomb used.

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[1] *Loc. cit.*

[2] The importance of thorough control of the conditions, especially of the degree of filling (the concentration of water in the total space within the bomb) and the temperature, has been demonstrated in a previous paper (Morey and Niggli, THIS JOURNAL, 35, 1086–1130 (1913).

[3] Procured from the Halcomb Steel Co., Syracuse, N. Y.

this hole is enlarged at the top so as to receive the parts by which closure is effected. For about $^1/_4$ inch above the shoulder, at *D*, the hole is cylindrical; above this up to where the screw thread is cut it tapers slightly, so as to allow the plunger to be more easily unseated. Strong threads of the type shown are cut in bomb and plug, the end of each of which is suitably squared off so as to allow one to place the bomb in a vise and screw the plug down hard by means of a wrench.[1]

Between the screw plug and plunger is a steel washer which ensures that the plunger does not rotate while the plug is being screwed down. The lower part of the plunger fits tight into the bomb at *D*; its upper part is a $^1/_2$ inch rod, which passes with a clearance of about $^1/_{32}$ inch through washer and plug. The projecting portion of this rod is threaded and fitted with the nut *A*; the main purpose of this feature is to aid in unseating the plunger when the bomb is to be opened. There are several advantages in making the head of the bomb as shown, instead of making it in one solid piece. By having the plunger separate and separated from the screw plug by a washer, all turning moment on the copper washed *D* is eliminated, thus making it easier to obtain a perfectly tight closure. Another important point is, that if experiments are made in which on cooling there may be a residual pressure, one can first unscrew the plug slightly and then, by means of the nut *A*, unseat the plunger, thus, by relieving the pressure while plug and plunger are still securely held by the remaining threads, obviating any chance of accident from this source.

Imprisoned in the annular space between the plunger and the body of the bomb is the flat copper washer *D*, $^1/_{16}$ inch thick, by means of which the joint is made tight.[2] The washer is always softened by annealing in a flame before use. It is prevented from flowing either upwards or downwards into the chamber of the bomb by the special form given to the plunger, which, as noted above, is made to be a good fit into the bomb just above and below *D*. It is essential that the copper be imprisoned in such a manner, otherwise it will flow at the high temperatures and pressures, thus giving rise to a leak; which in hydrothermal work, as has been pointed out in a previous paper,[3] cannot be tolerated. As an additional precaution to insure a perfectly tight closure, two knife edges, (not shown in the figure), about 60° and $^1/_{64}$ inch high and of slightly different diameters, are turned, one on the shoulder of the bomb, the other on the corresponding portion of the plunger. In order to be able to bring out the washer with the plunger, instead of leaving it within the bomb (in which case its removal is difficult), the lower portion of the plunger, which projects into the chamber, is made not exactly cylindrical but is cut inward so as to form a truncated cone of slight angle.

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[1] A wrench 2 feet long suffices.

[2] This type of closure has for some time been successfully employed by Johnston and Adams as a means of holding in very high pressures.

[3] Morey and Niggli, THIS JOURNAL, 35, 1086–1130 (1913).

The charge is placed in a crucible *G* of gold, which rests on the bottom of the bomb. Experience has shown that under such conditions the charge (at least with neutral or alkaline solutions such as we are dealing with here) is not contaminated by the iron of the bomb, so that a lining is unnecessary. Moreover, this method, besides being cheaper and avoiding a difficult piece of construction, facilitates greatly the manipulation, both previous to, and at the close of an experiment; the product is readily accessible and can be quantitatively removed, thus insuring complete freedom from contamination.

Temperature Measurement.—Temperatures are determined by means of a thermoelement inserted in the hole *F*, $^1/_8$ inch in diameter, drilled longitudinally in the wall of the bomb, as shown in Fig. I. Elements of copper-constantan are generally employed; the electromotive force is measured on a direct reading galvanometer, whence, with the aid of an appropriate calibration curve, the temperatures are derived. In view of the massive construction of the bomb and enclosing furnace and of the mode and duration of an experiment, it seems probable that the temperature throughout the chamber is fairly uniform and that it is indicated satisfactorily by the thermoelement junction in the top of the hole *F*. Indeed, experiments have shown that there is no appreciable temperature differences at different levels within the thermoelement hole. The temperatures given are, therefore, accurate to $\pm 5°$ or better, an accuracy which is ample for the purpose in hand; moreover, what uncertainty there is can easily be reduced to $\pm 1°$ as soon as the occasion demands it.

Construction of the Furnaces.—The construction of the electrical resistance furnaces used is shown in Fig. II, which is drawn to scale. The resistance wire, of "nichrome," is wound on an iron pipe, *D*, from which it is insulated by three layers of mica composition, such as is used in electrical work. The size and amount of wire are different in different furnaces: one is wound with No. 18 wire to give 300° when placed directly on a 55 volt line, and takes 5.6 amperes to hold it at that temperature; another is wound with No. 16 wire to give 500° when placed directly on a 110 volt line, and takes 5.8 amperes to hold it at that temperature; the other two are wound with No. 16 wire and are used with outside resistance, thus enabling one to secure intermediate temperatures.

The thermal insulation of the furnace consists of loose magnesia, *E*, held in place by the sheet-iron shell *F*, and the asbestos end-pieces *C*; the latter are held in place by the annular iron end-pieces, *B*, which fit tightly on to a slight shoulder cut on either end of the iron pipe *D*. The whole furnace is mounted in a strap iron frame, *G*, fastened by screws to the annular end-pieces *B*. The frame is provided with trunnions, *I*, which are mounted on suitable bearings in a support (not shown in the figure); by this means the furnace may be rotated about a horizontal axis or inclined at any angle. This style of furnace is easy to construct and simple in operation; in case a heating element is burned out the furnace can be dismantled, the element replaced, and the furnace re-assembled in a short time.

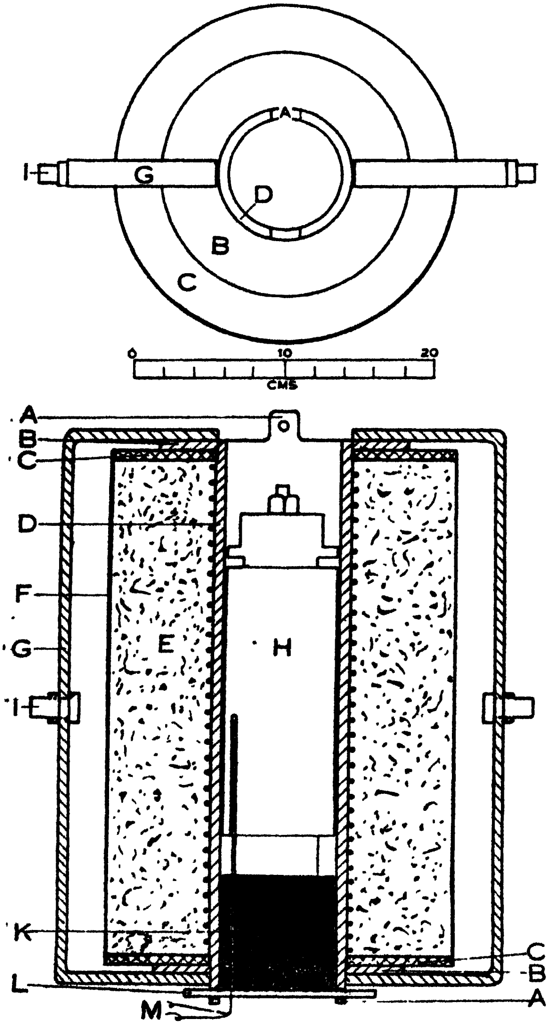

Fig. 2.—Diagram showing the construction of the furnace used.

The bomb *H* (shown in outline in Fig. 2) rests on a graphite plug, *K*, which is held in place by the rod *L*, passing through holes in the ears *AA* projecting from the main portion of the pipe *D*. A similar plug (omitted from the figure for the sake of clearness) fills the upper end of the tube. The thermoelement *M* passes through a hole in the bottom plug, as shown.

Materials Used. — The solid substances used in almost all the work consisted of finely pulverized glasses, which had been made by fusing mixtures of quartz and alkali carbonate in different proportions. The same components were also introduced into the bomb in other forms: the alkali as chloride, carbonate, hydroxide, and as silicate glass; the silica as quartz and as an amorphous precipitate; but these variations were altogether without influence on the resultant product. Since this is so, it is best to use the (anhydrous) glasses prepared as above described, not only because the components are intimately mixed and in a soluble and reactive form, but also because their use avoids any possible complications due to the introduction of other components.

Mode of Experiment.—A quantity of the alkali-silica mixture is weighed out into the gold crucible, a weighed amount of water is added and the crucible placed in the bomb, which is then closed and set in a furnace heated to the desired temperature. After being held at that temperature for a certain time, usually 20 hours, the bomb is cooled suddenly by plunging into water, opened and the crucible transferred to a desiccator; the entire operation can be completed within five minutes after withdrawal of the bomb from the furnace. The products are examined microscopically and chemically; crystals, if present, are, when possible, removed and analyzed.

Attention is directed to the following details of manipulation: All bearing surfaces on the washer and plug, the threads especially, must be well lubricated with a mixture of graphite and oil; the graphite by forming a coating on the steel surfaces prevents their sticking or welding together, as they will do if not lubricated. When a bomb is heated to a high temperature, *e. g.*, 500°, there may be sufficient difference in expansion between the steel and the copper so that the joint ceases to hold tight when the bomb is cooled down again, consequently in such a case care must be taken in the cooling of the bomb that the joint is always above the surface of the water; otherwise a little water may creep in during the cooling.

We shall now, after a few words on the analytical methods employed, describe the new crystalline products, and proceed to a discussion of the behavior of the hydrous alkali silicate glasses obtained in the course of the work.

Analytical Methods.—The analytical methods used in the course of the following work were simple. Water was determined by heating in an electric furnace at 800°; alkalies were weighed as chlorides, silica as SiO_2. The samples were decomposed by evaporating with HCl, three evaporations with intervening filtration being necessary for complete separation of alkali chloride and silica. The latter was always tested by evaporation with HF; all operations were carried out in platinum vessels. When but a small amount of material was available, as was the case in the analysis of the $K_2Si_2O_5$ crystals, the procedure was simplified. In this case it was necessary only to heat as above for the determination of H_2O, to evaporate twice with HF, followed by double evaporation with HCl to convert the fluorides to chlorides; since the only components present are water, alkali oxide, and silica, it is perfectly admissible to calculate the latter from the loss in weight.

Crystalline Products.

'*Potassium Hydrogen Disilicate.* $K_2O.H_2O.4SiO_2$, or $KHSi_2O_5$.—When an anhydrous potassium silicate glass is heated with water, the product obtained depends on the temperature, amount of water present (pressure), and concentration-ratio alkali oxide/silica in the sample of glass. If, for example, 2 grams of a glass of the composition $K_2O.2SiO_2$ is heated with 2 grams H_2O[1] at 400°, the product is a clear, hard, homogeneous, *hydrous* glass. If, however, the amount of water is reduced to less than 1 gram, the product is a mixture of hydrous glass and crystals. The crystals obtained under these conditions can be freed from adhering glass by leaching with hot water without affecting the sharpness of the crystal angles. The same crystals have been repeatedly obtained under a wide range of experimental conditions; at temperatures ranging from 200–450°, from glasses ranging in composition ratio from K_2O/SiO_2 to $K_2O/5SiO_2$, also when the original components were potassium carbonate and silica. Analysis of the crystals, in which each component was determined directly, yielded the following results:

	K_2O.	H_2O.	SiO_2
Found....................	26 71%	5 11%	68 16%
$K_2O.H_2O.4SiO_2$ requires.....	26 65%	5.10%	68.25%

The crystals then have the composition $K_2O.H_2O.4SiO_2$, and are, therefore, by analogy with the compounds to be described later, considered to be potassium hydrogen disilicate, $KHSi_2O_5$. This compound crystallizes readily in orthorhombic crystals,[2] the density of which is 2.417 ± 0.002,[3] at room temperature, referred to water at 4°. The crystals are not readily affected by water, even by treatment at 100° for several hours; when heated with dilute hydrochloric acid they are decomposed, leaving a birefringent residue containing only silica and water.[4] The vapor pressure of the water in the crystals is very slight; they can be heated in air to 350° without losing in weight, but the loss becomes appreciable at 450°.

Potassium Disilicate, $K_2O.2SiO_2$ or $K_2Si_2O_5$.—When anhydrous potassium silicate glass of the composition ratio $K_2O/2SiO_2$ is heated at about 450°, with an amount of water insufficient to give complete solution, crystals are formed the optical properties of which, so far as determinable, are identical with those of the compound $K_2O.2SiO_2$ found by Niggli.[5] These crystals, unlike those of $KHSi_2O_5$, break down immediately in water, and absorb moisture very rapidly from the air. On this account it has proved impracticable to separate the crystals from adhering glass sufficiently well to provide satisfactory material for analysis, or to make measurements on the goniometer. In one case, however, the crystals were so large that they could be separated from most of the hydrous glass by careful selection; the product was still contaminated by a small amount of hydrous glass, and weighed only 0.0717 gram. Analysis of this material yielded the following results:

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[1] The data given refer, of course, to a bomb of the capacity (about 75 cc.) given above.

[2] See crystallographic description by C. N. Fenner, *postea*.

[3] Determined for me by H. E. Merwin by the method described in *Am. J. Sci.*, **32**, 425–28 (1911).

[4] Cf. Rinne, *Neues Jahrb. Min. Geol.*, **1**, 139–48 (1896). This question is being investigated further.

[5] Niggli, THIS JOURNAL, **35**, 1694–1727 (1913).

	Per cent. by wt.	Mol. ratio.
K_2O	39.5	1.000
SiO_2 (by diff.)	47.9	1.894
H_2O	2.6	...

The composition ratio of the original anhydrous glass in this experiment was 1 : 1, while that of the crystals is evidently close to 1 : 2; some amount of water and a slight excess of K_2O are to be expected from the circumstance that the crystals could not be entirely freed from hydrous glass. This analysis is not absolutely conclusive, but the correctness of the formula $K_2O.2SiO_2$ is further demonstrated by two distinct lines of argument. First, this product, obtained from hydrous solutions in the neighborhood of 500°, is identical with the product obtained from dry melts in the neighborhood of 1000° by Niggli. Second, evidence obtained in the course of an extensive series of experiments on the temperature-pressure-solubility relations in the system $K_2O:SiO_2:H_2O$ points to the formation of this compound; this evidence will be presented in a later paper. The range within which this compound is stable is now being investigated; present experience indicates, in general, that at higher temperatures it is more stable than $KHSi_2O_5$, and that excess of potash is more favorable to its stability at lower temperatures than is excess of silica.

Sodium Disilicate, $Na_2O.2SiO_2$, or $Na_2Si_2O_5$.—When anhydrous glasses composed of Na_2O and SiO_2 are used in place of potassium silicate glasses, the products obtained are quite different. When a glass of the composition ratio Na_2O/SiO_2 is heated with considerable water above 400°, a homogeneous glass can be obtained, as in the potassium system, though the sodium systems have a considerably smaller solubility than the corresponding potassium systems.

When, however, a glass of the above composition ratio is heated at 300° with an amount of water insufficient to give complete solution, crystals are obtained which, in optical properties,[1] resemble $KHSi_2O_5$ and $K_2Si_2O_5$ and which resemble the former compound also in that they can be purified by leaching with water; but on prolonged contact with cold water they are decomposed, leaving a residue of hydrous silica. An analysis in which each component was determined directly, made with a sample of selected crystals of this compound, weighing 0.1701 gram, yielded the following results:

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[1] See crystallographic description by Fenner, *postea*.

	Per cent. by wt.	Mol. ratio.
Na_2O	33.69	1.000
SiO_2	65.52	1.999
H_2O	0.67	...
	99.88	

This compound is, then, sodium disilicate, $Na_2Si_2O_5$, analogous to the above potassium salts. It was also obtained at higher temperatures when using glasses whose composition ratio Na_2O/SiO_2 was less than unity.

Sodium Metasilicate, $Na_2O.SiO_2$, or Na_2SiO_3.—A second crystalline compound formed in the system $Na_2O : SiO_2 : H_2O$ is the metasilicate, Na_2SiO_3. When a glass of the composition ratio Na_2O/SiO_2 is heated with water at temperatures above 400°, crystals are formed whose isolation is difficult because they are decomposed very rapidly by water. Because of this circumstance the separation of pure unattacked crystals was not possible, but that they are anhydrous sodium metasilicate follows from several distinct lines of argument. First, when a glass of the composition ratio Na_2O/SiO_2 is heated at 500° with but a small amount of water, the product is wholly crystalline and practically anhydrous. Second, in some experiments in which more water was used, masses of crystals were obtained, together with a thick viscous solution. The crystals were freed as well as possible from the very viscous solution by pressing between filter paper; yet under the microscope they still showed a thin coating of solution. Analysis of a sample of these crystals weighing 0.1397 gram yielded the following results:

	Per cent. by wt	Mol. ratio.
Na_2O	49.72	1 000
SiO_2	47.87	0 990
H_2O	2.65	...
	100.24	

The crystals are evidently anhydrous sodium metasilicate; the small amount of water present, and the slight deficiency in silica, are to be ascribed to the presence of the small amount of viscous solution mentioned above. Third, the optical properties of these crystals separating from aqueous solution at about 500° appear to be identical with those of the crystals of anhydrous sodium metasilicate obtained from dry melts by Niggli.

The "Solubility" of the Alkali Silicates—As we have noted above, $KHSi_2O_5$ and $Na_2Si_2O_5$ are not readily affected by water, while $K_2Si_2O_5$ and Na_2SiO_3 are decomposed very rapidly. But from these facts one can draw no necessarily valid conclusions as to their real solubility, *i. e.*, as to the equilibrium between a solid of definite composition and the same substance in a solution saturated with it. The process is one of decomposition, the rate of which differs from one to another of the above four substances; it may be that the real solubility is roughly parallel to the rate of decomposition, especially when the latter is small, but this kind of reasoning must be employed with caution. This topic will be reverted to when the equilibrium relations at high temperatures shall have been more definitely ascertained.

General Remarks.—Attempts to prepare the compound $NaHSi_2O_5$, analogous to $KHSi_2O_5$, were unsuccessful, as were also all efforts to obtain crystals of K_2SiO_3. In this connection it is interesting to note that Niggli[1] found that at higher temperatures in the systems $K_2O-SiO_2-CO_2$ and $Na_2O-SiO_2-CO_2$, the stable alkali silicates are; in the potash system, $K_2Si_2O_5$ and K_2SiO_3; in the soda system, Na_2SiO_3 and Na_4SiO_4; increase in temperature in both cases favors the second form. This is in complete harmony with the hydrothermal results; in the potash system at the lower temperatures $KHSi_2O_5$ is stable and increase of temperature favors first $K_2Si_2O_5$, then (presumably)[2] K_2SiO_3; in the soda system at lower temperatures $Na_2Si_2O_5$ is stable, and increase of temperature favors first Na_2SiO_3, then (presumably)[2] Na_4SiO_4.

Remarks on the Disilicates.—The ease with which the disilicates of sodium and potassium can be formed hydrothermally is in striking contrast to the rarity of the occurrence of minerals which can, with any degree of certainty, be considered essentially as disilicates, that is, as salts of the hypothetical acid $H_2Si_2O_5$. The only mineral that is unquestionably a disilicate is rivaite, $(Ca, Na_2)\ Si_2O_5$, described recently by Zambonini,[3] which occurs very sparingly among the ejected blocks at Vesuvius. The hydrous minerals okenite and apophyllite furnish a ratio of CaO/SiO_2 which is that of a disilicate, the composition of the latter being somewhat complicated by the presence of potassium and of more or less fluorine. Both of these may possibly be regarded as hydrated disilicates. In the text-books the very rare petalite, $LiAl(Si_2O_5)_2$ and milarite, $HKCa_2Al_2(Si_2O_5)_6$ are cited as disilicates, as are the zeolites ptilalite and mordenite, if we accept Clarke's interpretation of their constitution. All of these, however, contain alumina, and there is at present no assurance that it would not be equally rational to regard them as derivatives of aluminosilicic acids.

Non-crystalline Products.

Preparation of Solid and Pasty Glasses.—When alkali silicate glass is heated with water, the product obtained depends on the temperature, composition ratio alkali oxide/silica in the original glass, and concentration of the water (pressure). The quantitative relations of these factors have not yet been ascertained, but a number of interesting qualitative observations have been made. When, for example, about 2 grams of an anhydrous glass of the composition ratio $K_2O/2SiO_2$ is heated with from 1–5 cc. water, the cooled product is a hard homogeneous glass containing considerable water (from 8 to 25%), the amount depending on the temperature and initial concentration ratios of the components. As the amount of water present is increased, the amount in the glass increases, in general accord with Henry's law. As the water content of the glass increases above 25%, the product passes gradually, and continuously, from a hard, brittle glass to a very stiff paste and finally to a very viscous solution resembling ordinary water glass. This is a striking illustration of the fact that a glass is merely a supercooled liquid.

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[1] P. Niggli, THIS JOURNAL, **35**, 1693–1727 (1913).

[2] Inferred from analogy with the results obtained by Niggli.

[3] F. Zambonini, *Atti accad. Sci. Nap.*, **12**, No. 12, 16 (1912).

That the hard glasses were liquid at the temperature of the experiments was proved in a number of ways. One way was to tip the bomb to one side, to an angle of about 15°, while heating, and to the other side while cooling; the glass was found to be collected on the side of the crucible which was lower during the cooling. When the concentration of the water was reduced to such an extent that some crystals were formed, they remained on the side of the crucible that was lower during the heating, while the solution in contact with them flowed away and froze solid on the side that was lower during the cooling.

It is, therefore, established conclusively that liquid solutions, containing water and alkali silicate, may exist in equilibrium with solid and vapor at temperatures up to 500°. It should also be pointed out that these hydrous glasses, liquid at the temperature of the experiment, may be regarded as fused mixtures, the melting point of the alkali silicate having been greatly lowered by the addition of water. For example, $K_2Si_2O_5$ melts at about 1015°, but addition of about 8% of H_2O[1] lowers its melting point to about 500°. It is probable that the system alkali silicate and water belongs to the type in which the solubility curve is not intersected by the critical curve;[2] but discussion of this phase of the problem is postponed until quantitative experimental results can be presented in detail.

Preparation of Pumiceous Glasses.—The glasses just described were obtained under the previously mentioned experimental conditions, that is, the gold crucible containing the charge was placed in the bottom of the chamber of the bomb, and cooling was effected by plunging the bomb suddenly into cold water, bottom first; under these conditions rapid cooling results, with the charge cooling as rapidly as, or more rapidly than, the vapor phase above. If, on the other hand, the crucible is supported near the top of the chamber, in such a manner (*e. g.*, on a porcelain tube) that its heat is conducted away less rapidly, the phenomena are very different. In this case the wall and vapor space are cooled more rapidly than the water-containing mixture in the crucible; consequently rapid diminution of the total pressure sets in, as a result of which the water in the liquid mixture suddenly expands, carrying with it, and at the same time freezing, the non-volatile portion of the charge. This produces a light, porous pumice of nearly anhydrous material. In other words, when the solution is cooled without release of pressure the product is a clear, homogeneous glass; when the total pressure in the bomb is suddenly diminished, the outburst of vapor causes the formation of pumiceous material.

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[1] It is evident that the system will be at the pressure corresponding to the vapor pressure of the solution; reduction of pressure at constant temperature will result ultimately in solid and vapor.

[2] Cf. Morey and Niggli, THIS JOURNAL, 35, 1086–1130 (1913), and the papers by Smits and by Niggli, referred to therein.

Behavior of the Hydrous Glasses when Heated in Air.—A noteworthy property of the clear, homogeneous, hydrous glasses is exhibited when they are heated in air. If a fragment of this glass the size of a pea is placed in a 30 cc. crucible and heated over a flame, the substance swells enormously, often overflowing the crucible,[1] the swelling continuing until most of the water has been driven off. The resulting sponge, the general appearance of which is similar to that of the pumiceous glasses described above, is composed of vesicles of alkali silicate glass, often with walls thin enough to show interference colors.

Crystallographic and Optical Properties.

By C N Fenner

Potassium Hydrogen Disilicate, $KHSi_2O_5$.—The crystals obtained were generally of fair size and in one instance sufficiently large for goniometric measurements; crystal outlines well developed. The habit of the crystals used for goniometric work is shown in Fig. 3. Measurements gave the following results: $001 \wedge 100$, 90° 0′; $100 \wedge 110$, 52° 32′; $110 \wedge \bar{1}10$, 74° 56′. In other preparations additional faces were sometimes present, especially macro- and brachy-domes (101 and 011), but in such cases the crystals were too minute for goniometric manipulation. Measurement with the microscope gave for $100 \wedge 101$, 60°–62°.

The habit of the crystals varied considerably. Commonly they were elongated parallel to the vertical axis, but it was not unusual for them to show tabular flattening parallel to 001 or to 100. Cleavage was well-developed parallel to front and side pinacoids.

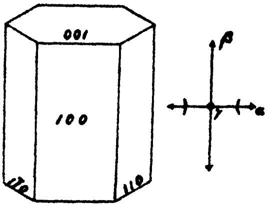

Fig. 3.—$KHSi_2O_5$.

The optical orientation is shown in Fig. 3. As indicated, the crystals are biaxial, positive. The refractive indices, as determined by the immersion method, vary somewhat in different preparations, perhaps owing to a slight solvent action of water in abstracting K_2O; $\alpha = 1.480 - 1.495$, $\beta = 1.530 - 1.535$; the higher values are probably more nearly correct. Average of a number of determinations of optic axial angle give for 2E $69^1/_2°$. The crystals are evidently orthorhombic.

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[1] Barus, *Am. J. Sci.*, [4] 9, 161–75 (1900), has described a similar phenomenon, which doubtless is to be explained in the same way.

Friedel and Sarasin,[1] in hydrothermal experiments, obtained a hydrated silicate of potassium, whose crystallographic properties agree closely with the above.

Potassium Disilicate, $K_2Si_2O_5$.—The crystals of this compound are difficult to work with, as they deliquesce rapidly and also enter into reaction with the immersion liquids. Some of their properties have been described in connection with a previous investigation by P. Niggli.[2] The crystals obtained in the present investigation were rather larger, and at times were free from any adherent material, such as glass. It was possible, therefore, to obtain additional information. In a number of preparations the crystals were sufficiently large for goniometric work, but their hygroscopic character prevented such determinations being made. Measurements were, therefore, confined to those which could be made with the microscope.

The crystals showed tabular habit, and under a binocular appeared as pearly scales, similar to Fig. 4. The cleavage parallel to the flat face is micaceous. There is also a strong cleavage parallel to the axis γ and another less well developed parallel to β. Frequently, contact with the index liquid develops a reticulated effect approximately parallel to α. The crystal faces bounding the plates are shown in Fig. 4, but the predominance of one or another set of faces varies among different crystals, so that the outline may become quite different. Frequently they are lozenge-shaped. The crystals lying upon the flat face show the emergence of an acute negative bisectrix. Axial angle is rather large (just beyond limits of field of an objective having numerical aperture of 0.95). Indices of refraction are a little uncertain because of reactions with the immersion liquids, but β is very close to 1.500. The crystals are apparently orthorhombic.

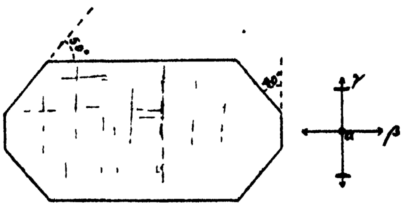

Fig. 4.—$K_2Si_2O_5$.

Sodium Disilicate, $Na_2Si_2O_5$.—Usually in scaly crystals, of form shown in Fig. 5; very pearly lustre on face 100; cleavage micaceous parallel to 100, good parallel to axis γ. A number of crystals were measured on goniometer, but signals were multiple or indistinct, and results are only approximate. Values obtained were: $110 \wedge \bar{1}10 = 31^1/_2°$; $011 \wedge 0\bar{1}1 = 60°$. Habit sometimes elongated as shown, sometimes as nearly regular hexagons. Parallel extinction; negative optical character. Average of a number of measurements of optic axial angle gave 2 E = 105°. Indices of refraction $\alpha = 1.500$, $\beta = 1.510$, $\gamma = 1.515$.

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[1] Friedel and Sarasin, *Bull. soc. min.*, 4, 171 (1881).

[2] P. Niggli, THIS JOURNAL, 35, 1693 (1913).

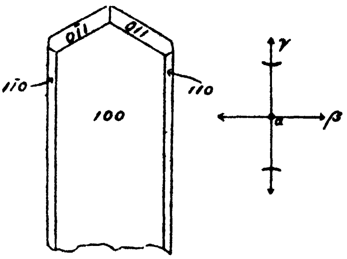

Fig. 5.—$Na_2Si_2O_5$.

Sodium Metasilicate, $NaSi_2O_3$.—These crystals rarely showed good crystal outline. They were usually more or less acicular, with fibrous cleavage parallel to elongation. These forms showed parallel extinction, and elongation was always γ; α was perpendicular to elongation. To judge from the manner in which the brushes of the optic figure disappeared upon rotation of the stage, γ is the acute bisectrix and the crystals may be uniaxial. As the compound is soluble in water the crystals could not be isolated from the pasty glass in which they were imbedded. The mean index of refraction was about 1.510. In one preparation well-formed individual crystals appeared, which were believed to be the same compound, though this is not quite certain. These were perfect hexagonal prisms, terminated by pyramids. The crystals lay upon their sides and gave an optic figure perpendicular to one of the axes of elasticity. The brushes always disappeared in the direction of elongation, which was γ. The same sort of figure was obtained when the crystals were rolled over in the thick mother liquor so as to rest upon another side, so that the mineral was probably uniaxial, positive. The interior angle of the terminating pyramid of these crystals was about 126°.[1]

Summary.

Hitherto, no well-defined crystalline silicates of potassium or sodium have been known. Several hydrated forms of sodium metasilicate have been described, but require further investigation, since their composition and range of stability are uncertain. None of these hydrated forms appeared in the course of the present investigation, which deals with the relations of the silicates of potassium and sodium with water at high temperatures and at the consequent high pressures.

In the investigation of such hydrous systems at high temperatures, reproducible results can be attained only if the conditions of experiment are carefully defined and controlled; in especial the concentration (pressure) of the water must be definite—in other words, leaks cannot be tolerated. The apparatus and methods described in the foregoing pages fulfil the various requirements admirably; in a series of over 200 experiments no sign of leak has been observed.

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[1] Compare crystals of Na_2SiO_3 obtained from fusion by P. Niggli, This Journal, 35, 1693 (1913).

Four new crystalline alkali silicates—namely, $K_2Si_2O_5$, $KHSi_2O_5$, $Na_2Si_2O_5$ and Na_2SiO_3—have been prepared. Of these the first three are derivatives of disilicic acid; they all form orthorhombic crystals, but differ markedly in their behavior toward water. $K_2Si_2O_5$ is quickly attacked by water, $Na_2Si_2O_5$ less readily, while $KHSi_2O_5$ may be left in contact with water, even for some hours at 100°, without appreciable decomposition. The fourth compound is anhydrous sodium metasilicate, which is readily attacked by water; this compound has been known heretofore only as a somewhat indefinite hydrate.

In addition to the crystalline products, a series of hydrous glasses was obtained. These glasses are merely supercooled liquids, each of which represents the composition of a solution unsaturated under the conditions of experiment. They are perfectly hard, even though they contain up to 25% water; when heated in the air they lose their water, swelling up in the process in a sponge-like structure often with extremely thin vesicular walls.

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RECENT WORK IN INORGANIC CHEMISTRY.

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While the past twelve months have witnessed no startling developments in the field of inorganic chemistry, there has been no diminution in volume of work. Perhaps the two strongest tendencies are (1) to go over old work with modern methods and in the light of modern theories, with resulting confirmation or otherwise, and (2) to project new theories into wider fields to test their applicability and breadth. This has been notably the case with Werner's ideas in their application to complex compounds. Here there has been no such remarkable discovery as that of two years ago regarding the optical isomerism of inorganic compounds, nevertheless there has been an increasing use of these ideas in the explanation of the constitution of compounds which are inexplicable by any of the older theories; as for example Weinland's work on basic salts and that of Rosenheim on the poly-acids of molybdenum, tungsten, etc. Continuing his work on the ferric acetates, where the dominating kation contains three ferric atoms and six acetate groups (hexacetato-triferri base), Weinland has studied (*Z. anorg. Chem.*, **80**, 402) the compounds formed by the action of pyridine on a solution of a ferric salt in anhydrous acetic acid. Different compounds are formed according to the proportions used, but the characteristic point is that the ratio of iron to acetate in the kation changes with the entrance of pyridine from 3 : 6 to 2 : 3. A typical formula is $\left(Fe_4\left\{\begin{matrix}(CH_3CO_2)_6\\ 3\ \text{pyr}\\ (OH)_2\end{matrix}\right.\right)^{++++}$, though other kations are formed containing

4, 5, and 6 molecules of pyridine. In a later paper (*Ber.*, **46**, 3144) Weinland gives the action of sodium formate on ferric salts. When the formate is in large excess the salt of the hexaformato-ferric acid is obtained, $Na_3Fe(HCO_2)_6$, corresponding to ferricyanides, etc. This anion is pale green, resembling in this respect the ferrioxalate ion, $Fe(C_2O_4)_3$. If, however, in mixing the ferric salt and sodium formate, the latter is not in large excess, the kation of a hexaformato-triferri base is formed, $(Fe_3(HCO_2)_6)(OH)_3$. This is deep red and is the cause of the color when a formate is added in small quantities to a ferric solution. In intermediate solutions there is present the equilibrium,

$$3Na_3Fe(HCO_2)_6 + 2H_2O \rightleftharpoons \underset{(OH)_2}{(Fe_3(HCO_2)_6)}(HCO_2) + 9NaHCO_2 + 2H.HCO_2.$$

Since both acid and base are trivalent, a number of different salts containing both can be obtained, as for example: $(Fe_3(HCO_2)_6)(Fe(HCO_2)_6)$ and $\underset{(OH)_2}{(Fe(HCO_2)_6)_3}(Fe(HCO_2)_6)$. By using a large excess of sodium formate with chromium salts a hexaformato-chromate, $Na_3Cr(HCO_2)_6$, was obtained. This salt is green-violet and corresponds to the chromoxalates, perhaps more properly named, oxalato-chromates. In this connection mention may also be made of the ferric urea compounds described by Barbieri (*Atti accad. Lincei, Rome*, [5] **22** i, 867) which have the formula $Fe(CO(NH_2)_2)_6.X_3$, and are isomorphous with the corresponding chromium urea compounds, but less stable; and of the compounds of platinous chloride with aminoacetal described by Tschugajew (*Compt. rend.*, **155**, 1021). These have the formulas, $Pt(2A)Cl_2$, $Pt(4A)Cl_2$, and $Pt(2A.\text{-}2NH_3)Cl_2$ ($A = NH_2.CH_2.CH(OC_2H_5)_2$). Isomers to the last salt could not be obtained. The compounds of platinum with thio-bases will be considered farther on. The work of Rosenheim has been extended to include the dekamolybdates (*Z. anorg. Chem.*, **79**, 292), which seem to exist in two isomeric forms, differing greatly in solubility, and the organic arseni-molybdates (*Ber.*, **46**, 539), or again better called from their constitution, molybdato-alkyl (or phenyl) arsinates. Guanidinium salts proved themselves here, as frequently in the study of other polyacids, best suited to the study of the basicity of the compounds, and were formed by adding guanidinium chloride to the solution of cacodylic or other arsinic acid saturated with molybdic oxide. It is interesting to note that in these polymolybdic acids a portion of the molybdic trioxide or heptoxide can be replaced by alkyl, phenyl, or even substituted phenyl groups. Another line of investigation which has at least an indirect bearing on Werner's ideas is that of Ephraim (partially reported last year) on "Nebenvalenz," perhaps most correctly translated *secondary valence* (*Z. physik. Chem.*, **81**, 513, 539; **83**, 196; *Ber.*, **46**, 3103) Ephraim has studied particularly the ammonia compounds (ammoniates) of the halides of bivalent metals, and has endeavored to measure the strength of the secondary valence which holds the ammonia by measuring the vapor-pressure of these ammoniates. He finds that the affinity of ammonia for the salt is the greater, the less the atomic volume of the central metal; the expression $\sqrt[3]{v}.\sqrt[3]{T}$, in which v is the atomic volume of the metal and T the dissociation temperature, being nearly a constant. There is also a constant relation between the dissociation-temperatures of most of the ammoniates of chlorides and those of the corresponding bromides, iodides, and sulfates. The ammoniates appear to differ from hydrates in that the ammonia is given off molecule by molecule, while intermediate hydrates of salts are frequently lacking; but this Ephraim thinks is merely apparent, and that it is only owing to their solubility relations that all possible hydrates are not realized in solid form. Biltz, however (*Z. physik. Chem.*, **82**, 688) denies the conclusion which Ephraim has drawn from his experiments, that ammonia is given off molecule by molecule, and presents experimental evidence that $Ni(NH_3)_6Cl_2$ passes directly into $Ni(NH_3)_2Cl_2$ without the formation of any intermediate ammoniate. In his last paper, Ephraim compares the dissociation-temperature of ammoniates with that of ammonium salts, finding a marked similarity, and draws the conclusion that ammonium salts may be looked upon as ammoniates of hydrogen salts, *i. e.*, acids. This is, of course, what Franklin has already found to be true in respect to ammonium salts dissolved in liquid ammonia. Ephraim also finds a parallelism in the dissociation-temperature of phosphonium compounds, which may from this standpoint be written, $H(PH_3)Cl$, etc.

In determining whether a given salt is to be considered as "double" or "complex," Dhar (*Z. anorg. Chem.*, **80**, 43) would use molecular conductivity as a criterion, relying upon the fact that this is dependent on the velocity of the ions and the latter in turn is strongly influenced by the size of the ion. He presents the measurements of a long list of salts, which show that many of the complex ions are very stable even at great dilution. Ephraim, however, points out (*Fortschritte Chem.*, **8**, 198) that these results indicate merely whether the complex is stable in dilute solution, and not whether the complex really exists or not under other conditions, *e. g.*, at greater dilution or in other than aqueous solutions.

In the first of a series of studies on chemical crystallography (*J. Chem. Soc.*, **101**, 2484), Barker calls attention to the value of Werner's coördination theory in explaining many otherwise inexplicable anomalies of isomorphism. Among a number of examples cited we may note as examples: $CuTiF_6.4H_2O$, $CuCoOF_5.4H_2O$, $CuWO_2F_4.4H_2O$, which according to the coördination theory, would be written, $(TiF_6)Cu + 4H_2O$, $(Co^{O}_{F_5})Cu + 4H_2O$, $(W^{O_2}_{F_4})Cu + 4H_2O$; and $MnCl_2.4H_2O$, Na_2GlF_4, which would be written $(Mn4H_2O)Cl_2$, $(GlF_4)Na_2$. It seems rather remarkable that such a working out of the application of the coördination theory to crystallography has not been undertaken long ago. In this connection it is worth while to call attention to the plea of von Fedorov (*Z. Kryst. Min.*, **52**, 22) for a more complete study of the chemical molecule in its spatial relations, with reference to the crystal molecule and its symmetry.

In a Russian text-book (abstract in *Zentrbl. Min. Geol.*, **1912**, 758), Wernadski has given a table of 106 minerals which consist of native elements. The fact that 5% of all minerals are not stoichiometric compounds, but either free elements or homogeneous mixtures of elements, points to a peculiar chemical condition of the earth's crust. Many things favor a destruction of chemical compounds; as for example the fact that in volcanic extrusions many elements are in gaseous condition, a state peculiarly susceptible to the action of electric phenomena, of ultraviolet light and radioactive emanations; and the fact that in cosmic solutions, in which many elements are present in exceedingly minute amounts, there is no possibility of all being united in stoichiometric compounds. In every smallest portion of the earth's crust many, if not all, the elements may be found, when sufficiently exact analytical methods shall be devised. The concentration of these elements is infinitesimally low, and the author speaks of them as being in a *microcosmic mixture*. Most minerals composed of native elements are "rare," and altogether they make up hardly 0.1% of the earth's crust; still not less than 47 of the known elements occur in native condition. Possibly Wernadski's microcosmic mixture may prove to be identical with colloidal solid solution, or merely colloidal solution in the case of sea-water. This idea of a solid colloidal solution is brought out by von Veimarn in a paper on the condition of gold in gold quartz (*Z. Chem. Ind. Kolloide*, **2**, 287). Such quartz is milk-white and translucent and the gold must be in super-ultramicroscopic condition; this colloidal condition may be ascribed to the action of silicic acid as a protective colloid. We may also note that Merrill (*Am. J. Sci.*, [4] **35**, 509) has gone over much of his former work on the chemical constituents of meteorites, using most modern methods in searching for the elements present in minute quantity, and in each case using not less than 50 grams of substance. The following elements, heretofore supposed to be present, were not found: antimony, arsenic, gold, lead, tin, tungsten, uranium and zinc. The occurrence of platinum was placed beyond dispute, especially in the Perryville iron, where 4 mg. were found in 25 grams substance, as well as a minute trace of palladium. In this same iron 14 mg. of ruthenium and 28 mg. of iridium were found in 100 grams of substance. Traces of vanadium were found in two falls. In no case were barium, strontium or zirconium present. A paper by Chamberlain (*J. Geol.*, **17**, 534) on the gaseous content of rocks is an interesting contribution to cosmic chemistry. Space does not permit of complete abstraction, but a few points may be noticed. All rocks contain gases, the basic eruptives most in quantity. While some of this gas results from decomposition, some is present in an occluded condition (solution). This is very different in composition from the atmosphere. Of the gases, certainly H_2O and CO_2 were constituents of the original magma, and as these were liberated CO and CH_4 were also formed by interaction. Oxygen is found only in combined condition in rock masses of the earth. The earth interior is very poor in oxygen and the earth crust not extremely rich, for, as a whole, the crust is suboxidized. Atmospheric oxygen was of late appearance, formed from the decomposition of oxides, especially water, and was later increased by the decomposition of CO_2, after plant life had appeared. The hypothesis of a primary gas content of the earth interior is in accord with the planetesimal hypothesis.

An investigation of the most refractory oxides in the carbon resistance vacuum furnace has been carried on by Ruff (*Z. anorg. Chem.*, **82**, 373) both for the purpose of getting fixed normal temperature points, and also to determine the most refractory materials for high temperature work. Alumina was found to give a definite melting point of 2010° ± 10°, too low however for a very refractory material. The only other possibly definite points were the melting points of glucina at about 2525° and zirconia at about 2585°; but it is not yet certain that these remain entirely unreduced under the influence of the high temperature, low pressure, and reducing gases in the carbon tube. They are, however, entirely satisfactory as refractory materials. Magnesia is also refractory, fusing about 2550°, but volatilizes rapidly, and while lime has probably nearly as high a melting point it is even more volatile. Other oxides, such as ceria, yttria, thoria, and Cr_2O_3, were more or less converted into carbides before fusing. Work by Kaye and Ewen (*Proc. Roy. Soc. Lond.*, (*A*) **89**, 58) on the sublimation of metals at low pressure, carried out with iridium, copper, iron and tungsten, leads to the conclusion that vapors of two sorts are given off under the conditions of the experiments, (1) ordinary vapors of the gaseous element, and (2) a vapor of metallic particles passing off in right lines normal to the metallic surface, with a path one centimeter long in a vacuum. These particles appear to be electrically charged metallic particles, whereas the ordinary vapors are electrically neutral.

Passing from these more general investigations to those confined to single elements and their compounds, we follow the periodic table.

Group I.—In connection with measurement of the vapor pressure of metals by the dynamic method, von Wartenberg (*Z. Elektrochem.*, **19**, 482) noted that silver is appreciably more volatile in oxygen than in nitrogen, and attributes this to the formation of silver oxide at a high temperature. Although this oxide is unstable at low temperatures, owing to its high heat of vaporization it should be possible for it to exist at high temperature as a gas. From the equilibrium $4Ag + O_2 \rightleftharpoons 2Ag_2O$ it should be possible, according to the law of mass action, for some Ag_2O to exist at high temperatures when the oxygen concentration is great. The reviewer has found it possible to obtain PH_3 by leading hydrogen over (red) phosphorus at its volatilization point, and has also found, quite in analogy with the work of von Wartenberg, that RuO_4 can be detected in oxygen which has been led over metallic ruthenium at a high red heat, although RuO_4 decomposes with violence when heated to about 100°.

Group II.—Metallic glucinum has been prepared by Fichter and Jablczynski (*Ber.*, **46**, 1604) by the electrolysis of a fusion containing GlF_2 and NaF. The metal was obtained in crystalline form, but was covered with a thin film of oxide. This rendered the determination of its fusing point difficult, but it appears to be 1280° ± 20°. It volatilizes at above 1900°. The freshly filed metal is steel-gray and has a hardness of 6 7. Though brittle at ordinary temperatures, when heated it becomes ductile. Owing to its coating of oxide the metal appears to be resistant to reagents, but it is actually slowly acted on by boiling water. It is less attacked by 0.01 *N* HCl than magnesium but more than aluminum. Nitric acid (1.4) acts on it only when heated; and the same is true of 10% potassium hydroxide, while a 50% solution dissolves it in the cold. Its properties thus accord with its position as the first element of Group II.

In determining the vapor pressure of the hydrogen in CaH_2, Moldenhauer and Roll-Hansen (*Z. anorg. Chem.*, **48**, 137) found that, when the porcelain tube was lined with iron, the pressure differed according to whether pure CaH_2 or a mixture of CaH_2 with Ca was used. This could be accounted for by assuming the existence of a lower hydride, CaH. When an unprotected porcelain tube was used a different but constant pressure was obtained, and it was found that there was an evident slight volatility of the lower hydride and reaction with the porcelain. In reviewing this paper in the Fortschritte, Ephraim mentions that a hydride of calcium appears to exist which is volatile at ordinary temperatures, which Hoffmeister has also found in commercial acetylene. Edler finds (*Ber.*, **46**, 2264) that calcium hydride reduces barium sulfate according to the reaction $BaSO_4 + 4CaH_2 = BaS + 4CaO + 4H_2$, which is strongly exothermic. This reaction appears to be excellently applicable (*Z. anorg. Chem.*, **83**, 149) for the concentration of radium, for the mass after reaction is porous and dissolves readily in HCl. By using 1/1 *N* HCl any PbS and SiO_2 is left undissolved and the barium and radium can be fractionally precipitated by HCl gas, while calcium and any iron remain in solution.

Group III.—In 1912, Stock, for the first time, isolated two borides of hydrogen, $H_{12}B_6$ and $H_{10}B_4$, both exceedingly unstable compounds. The past year (*Ber.*, **46**, 1959) he has added another boride to these two, H_6B_2, which proves to be decidedly more stable, but so extremely sensitive to the presence of water that it has hitherto escaped discovery. Its recognition now is due to the fact that $H_{10}B_4$ decomposes spontaneously at ordinary temperature, and more rapidly when heated, into H_6B_2 and hydrogen, together with a small quantity of less volatile borides. The H_6B_2 is separated from any unchanged $H_{10}B_4$ by fractional distillation. The boiling point of H_6B_2 at atmospheric pressure is −87 to −88°, and its melting point is below −140°. Its density is 13.8, which is close to theory for the formula H_6B_2. It is fairly stable at ordinary temperatures, but decomposes slowly with the formation of solid borides. This decomposition is more rapid when the gas is heated. In this boride, the boron seems to be quadrivalent and the compound analogous to ethane. Its boiling point also corresponds to that of ethane (—90°); that of silico-ethane is —7°. Similarly, $H_{10}B_4$ may correspond to butane; its boiling point is 16° and that of normal butane 1°. In a later communication (*Ibid.*, 3353), Stock describes the volatile solid hydrogen boride which is formed when H_6B_2 is decomposed. Its formula, as determined by analysis and molecular-weight determination by freezing-point depression in benzene, is $H_{14}B_{10}$. It fuses sharply at 99.5° to a water-clear liquid which readily crystallizes again. It is fairly stable, being largely unchanged on passing through a tube heated to 400° (*in vacuo*), but on heating slowly above 200° it is, partially at least, converted into another boride which is insoluble in carbon bisulfide. $H_{14}B_{10}$ is soluble in alcohol, ether, benzene and especially in carbon bisulfide, and can be recovered from its solutions, but with great loss owing to its volatility. It is not acted on by water, in which it is insoluble, and scarcely attacked by concentrated nitric acid. The difficulty attending its production is partly realized when one considers that the yield from decomposing 1 cc. of H_6B_2 is 0.5 mg. In this decomposition two other solid borides were obtained, one soluble and the other insoluble in carbon bisulfide, but the quantity was too small for complete investigation. The former contains hydrogen and boron in a ratio of 4H : 5B, and is thus decidedly poorer in hydrogen than any of the other borides found. The other boride has a molecular weight (in benzene) of about 142, and thus probably contains 12 atoms of boron in the molecule. Stock has thus isolated altogether seven borides of hydrogen, five of which have been accurately studied and their formulas determined. The existence of three others has been noticed but they have been in too small quantities for any investigation, Since some of the borides prepared by Moissan and by Moody and Tucker contained carbon as carbide, or aluminum, Wedekind (*Ber.*, **46**, 1198, 1885) has used other methods for the preparation of borides, old and new.

In several cases success was attained by the use of the vacuum arc furnace, the electrodes being made of a mixture of boron with the desired metal, sufficiently fritted to conduct the current. In this way Zr_3B_4, VB, and UB_2 were prepared. WB_2 was also obtained, corresponding to that prepared by Moody and Tucker, but borides of molybdenum and titanium could not be made in pure condition. CaB_6 was prepared by the reduction of calcium borate by metallic calcium in an iron tube. It resembles that obtained by Moissan in the electric furnace, except that its color is light brown, while that of Moissan was black, doubtless owing to impurities. In the borides of this type there seems to be present a very stable group, B_3, and it is possible that a hydrogen boride with formula HB_3 is present in the solid borides obtained by Stock.

A new contagious disease of metals is described in the *Chemical News* (**108**, 4) which affects the alloy of 97% aluminum and 3% copper used by the French government for the manufacture of helmets and other military objects. The disease is epidemic and spreads by contact from one object to another, corroding the metal and making holes in it. The metal looks as if attacked by eczema, and thus far no remedy has been found.

Group IV.—In discussing, a year ago, the combustion of coal, Rhead and Wheeler drew the conclusion that both CO and CO_2 are formed, and promised an explanation of this phenomenon. This has now appeared (*J. Chem. Soc.*, **103**, 461), and consists in the hypothesis that carbon absorbs oxygen with the formation of a carbon-oxygen complex, which is stable up to high temperatures, and which on decomposition under the influence of heat gives off both CO and CO_2. That this absorption of oxygen is not a mere physical absorption seems apparent from the fact that no gas is given off by merely diminished pressure, and that coal which has been highly heated does not absorb CO or CO_2. The composition of this carbon-oxygen complex, C_xO_y, depends upon the temperature at which it is formed; when this takes place at 300° the formula is $C_{100}O$, but it is not to be looked upon as a uniform chemical compound. While it is true that this hypothesis would satisfactorily account for the facts of the combustion of coal, the evidence presented in its support seems pretty meager. Methane has a strong tendency to decompose above 600°, but at this temperature, under ordinary circumstances, carbon is not deposited; but if a metal is present with which carbon has a tendency to unite which is stronger than its tendency to be deposited as elementary carbon, then a carbide will be formed. The lower the temperature the less tendency to deposit free carbon, but as lowering of the temperature decreases the velocity of the reaction, hydrogen may be mixed with the methane, diminishing the dissociation and allowing a higher temperature to be used. Hilpert and Ornstein (*Ber.*, **46**, 1669) have used this method of heating the metal in a current of methane and hydrogen, for the preparation and study of carbides. An analogous method, in which there is less trouble from concomitant deposition of carbon, consists in heating the metal in CO, the equilibrium being $2CO \rightleftharpoons C + CO_2$. In this case the tendency to deposit carbon decreases with the increase of temperature. At 1000°, with molybdenum, Mo_2C was the limiting carbide, while at 800° MoC was rapidly reached, but still more carbon was slowly taken up, with a probable limiting value of Mo_3C_4. At 600°, however, the limiting compound was, as at 1000°, Mo_2C. With tungsten below 900°, with methane, WC was quickly reached; at 1000°, with CO, W_3C_4 was the limiting compound. In the CO atmosphere tungsten was appreciably volatile (formation of a tungsten carbonyl?). This reaction for the formation of carbides would undoubtedly be strongly influenced by the heat of formation of the carbide, and in this connection it may be noted that this heat of formation has been determined by Ruff (*Ibid.*, 400) for Mn_3C, Fe_3C, and Ni_3C to be respectively, $+12.9 \pm 2.14$, -15.3 ± 0.2, and -394 ± 10 Cal. This substantiates the fact that Mn_3C undergoes no apparent change on cooling. Fe_3C can be obtained in 90% yield by rapid chilling, while it is difficult to preserve any Ni_3C even in great dilution and with most rapid chilling. Curiously, however, no carbide of definite composition could be obtained by Hilpert (*Ibid.*, 3479) on heating metallic manganese in methane. In pure methane the carbide mass contains upwards of 20% carbon, and in a mixture of equal parts methane and hydrogen 15% carbon. The saturation limits varied with the temperature to which the manganese was heated, but in no case did the mass present any simple atomic ratio. The reaction with acids also indicated that no derivatives of simple hydrocarbons were present. All of these manganese carbide masses are ferromagnetic. To the three compounds of carbon and nitrogen, cyanogen, paracyanogen of Gay-Lussac and Johnston, and the recently discovered carbon pernitride, NCN_3, of Darzens, is now to be added a fourth, C_3N_2, prepared by Pauly and Waltzinger (*Ber.*, **46**, 3129) by heating imidazole tetraiodide. This iodide, when heated in a vacuum, loses three atoms of iodine below 200° and the fourth at about 400°, leaving a mass which resembles soot, and bears a strong resemblance to animal charcoal. On heating to 800–900° it decomposes into cyanogen and carbon, and on heating with soda-lime gives off all its nitrogen as ammonia. While not identical with paracyanogen, it is evidently of similar nature. While it is insoluble in all indifferent solvents and infusible, the fact that it is formed quantitatively from $C_3N_2I_4$, as well as its chemical properties, indicates that it is a definite chemical individual.

By the action of metallic calcium on a mixture of silicon and aluminum, Reynolds (*Proc. Roy. Soc.*, (*A*) **88**, 37) has prepared a compound, $Ca(SiAl)_2$, which he calls calcium silical-cyanid, that is a cyanid in which the carbon is replaced by silicon and the nitrogen by aluminum. The compound is exceedingly stable and indifferent to oxygen even at high temperature but great interest must attach to it from the fact that when heated to a low redness in a current of *moist* oxygen it gives a compound, $CaAl_2Si_2O_8$, which in composition, appearance and other properties bears the closest resemblance to anorthite. Much interest must also attach to a compound which bears a relationship on one side to a complex silicate and on the other to a cyanide.

By the solution of potassium stannate in hydrofluoric acid Marignac obtained two distinct salts to which he gave the formula $K_2SnF_6.H_2O$. This has now been cleared up by Briggs (*Z. anorg. Chem.*, **82**, 441). When the fluo-stannate, best prepared by the method of Emich from $SnCl_4$, and KF, is dissolved in water the reaction is acid. On the addition of exactly one molecule of KOH the solution becomes neutral, and from it is crystallized the second salt of Marignac, in thin brilliant flakes, which have the formula $K_2SnF_5OH.H_2O$, a hydroxy-pentafluo-stannate. At 170°, water is given off and an anhydride, probably $K_4(SnF_5.O.SnF_5)$, formed, which, on solution in warm water, regenerates the original hydroxy-salt.

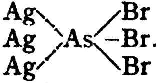
Group V.—The orange-yellow cloud-like luminescence observed when the electric discharge is passed through nitrogen at pressures from 1 to 10 mm. is ascribed by Strutt to an active modification of nitrogen. This is disputed by Comte (*Physik. Z.*, **14**, 74) who finds that when pure nitrogen is used the luminescence is reduced to a minimum, and ascribes the phenomenon to the reaction between nitrogen and a little oxygen present as impurity. The same view is held by Tiede (*Ber.*, **46**, 340). On the other hand, Strutt (*Physik. Z.*, **14**, 215) shows that in his experiments oxygen was practically absent, and that intentional additions of oxygen inhibit the phenomenon proportionally. Comte's results may have been due to impurities introduced in removing the oxygen. In a later article (*Proc. Roy. Soc.*, (*A*) **88**, 539), Strutt gives further details regarding active nitrogen and its reactions. With vapors of mercury, cadmium, zinc, arsenic, sodium and sulfur, nitrides are at once formed which are at once decomposed by water with evolution of ammonia. Carbon bisulfide gives a blue polymeric nitrogen sulfide, $(NS)_x$, and a polymeride of carbon monosulfide. Active nitrogen reacts with many organic substances, giving in almost every case hydrogen cyanide, but no cyanogen. None of these reactions would be characteristic of an oxide of nitrogen. The action of ozone on liquid ammonia at low temperatures would seem, according to Manchot (*Ber.*, **46**, 1089), to be analogous to that on the caustic alkalies, for here also an intense orange-red color is formed, which becomes pale when the temperature is allowed to rise to —65°. If a few drops of water are present the color is stable to a somewhat higher temperature. In perfectly dry non-aqueous solvents, when saturated with ammonia, no color appears on addition of ozone, even at very low temperatures, nor do liquid organic amines give a color with ozone, although there is an evident reaction. It seems probable that the reaction of ozone with ammonia is really with the hydroxide, NH_4OH, which is stable at low temperatures and is more closely akin to KOH and NaOH than are dimethyl- and trimethylamine. Some fifteen years ago Melikoff and Pissarjewski prepared, by the action of ammonia on hydrogen peroxide, an ammonium hydroperoxide, NH_4O_2H. In repeating their work, D'Ans and Wedig (*Ber.*, **46**, 3075) led dry NH_3 into a 98% solution of hydrogen peroxide in absolute ether at —10°. At first beautiful clear crystals appear, which are the hydroperoxide, m. p. 14°, but on further addition of NH_3 these fuse and there is formed at the bottom of the flask a heavy oily layer. On cooling to —40° this oil freezes to a crystalline mass. This mass was washed with ether in a specially constructed apparatus, cooled by a carbon dioxide-ether mixture. The pure crystals thus obtained are ammonium peroxide, $(NH_4)_2O_2$. On warming they begin to lose ammonia, forming NH_4O_2H, and melt at about —2°. They are somewhat soluble without decomposition in cold ether.

A study of the fixation of nitrogen by a mixture of barium oxide and carbon has been carried out by Ewan and Napier (*J. Soc. Chem. Ind.*, **32**, 467). Fixation appears to take place according to one or both of the two reactions, $BaO + 2C + N_2 \rightleftharpoons BaCN_2 + CO$, and $BaO + 3C + N_2 \rightleftharpoons$

$Ba(CN)_2 + CO$. Both of these reactions are reversible but were not found to be appreciably affected by any catalytic agents, although the presence of a little (up to 11%) K_2CO_3 lowered the reaction temperature 10 to 20°. The second reaction is connected with the reaction $Ba(CN)_2 = BaCN_2 + C$, which does not appear to be reversible. When nitrogen is led over the baryta-carbon mixture at 1100°, it is rapidly absorbed until nearly half the baryta has been converted into a nitrogen compound. The further absorption of nitrogen goes on with extreme slowness, although it would seem that no true equilibrium would be reached (the nitrogen supply being continuous and the CO removed) until all the barium is combined with nitrogen. The best that could be attained was 57% yield, and this only after 80 hours' heating. The rather sudden impeding of the reaction seems to be due to the formation of a compound, $BaO.Ba(CN)_2$, in which the BaO is far less active than when free; this would also seem to account for the fact that there is even at 1150° no volatilization of the $Ba(CN)_2$, which by itself is somewhat volatile at a decidedly lower temperature. Another reaction which must possibly be taken into account is $BaO + 3C \rightleftharpoons BaC_2 + CO$. The equilibrium pressure of this reaction at 1200° is 1 mm., hence it is probable that barium carbide is hardly to be considered an intermediate product in the absorption of nitrogen. On the other hand, in the reaction between lime, carbon and nitrogen, the carbide is probably an intermediate product of importance. The fixation of nitrogen by aluminum has been studied by Fichter (*Arch. Sci. phys. et nat., Genève*, [4] **35**, 369; *Z. anorg. Chem.*, **82**, 192), Fraenkel (*Z. Elektrochem.*, **19**, 362), and Wolf (*Z. anorg. Chem.*, **82**, 159). Fichter finds that the affinity of aluminum for nitrogen is very considerable. When a nickel tube filled with aluminum powder is heated to 700° and nitrogen led over it, the temperature rises suddenly to 820° and nitrogen is rapidly absorbed. The temperature in the interior of the mass rises to above 1300°. The product contains some particles of aluminum which have been unacted on, but by powdering and again heating in nitrogen a pure product can be obtained which has the formula AlN. The affinity of aluminum is so great that when air is led over the heated metal, some nitride is found in the oxide formed. Water easily decomposes the nitride with the formation of ammonia, and in moist air the nitride always has an odor of ammonia. While hydrochloric acid acts readily on the nitride, if metallic iron and aluminum are present as impurities they can be sublimed away by heating in a stream of perfectly dry HCl gas, leaving the AlN pure. By long action of HCl gas, or at a higher temperature, the nitride is itself attacked. By heating with alkalies and carbon the nitrogen of the nitride is converted, but not completely, into cyanide nitrogen. In order to obtain the nitride by the action of nitrogen on a mixture of alumina and carbon, the temperature must not rise above 1800–1850°, or the oxide will melt and carbide be formed, which inhibits the reaction. The reaction, $Al_2O_3 + N_2 + 3C \rightleftharpoons 2AlN + 3CO$, first carried out by Serpek, has been studied by Fraenkel, who finds that when soot is used the reaction begins at 1400° and increases rapidly in velocity with rising temperature, while the nitrogen pressure has little influence. The reaction is inhibited by mixing CO with the nitrogen, and is reversible. At 1500° and 760 mm. equilibrium is reached with 25–40 volume per cent. CO; at 1600° with 50–65%. Above 1500° carbide begins to be formed. The velocity of the reaction is strongly influenced by the nature of the carbon used. Wolf finds that the purity of the aluminum plays an important part in its reaction with nitrogen, and that by using aluminum bronze it was possible to convert only 2.47% of the aluminum into the nitride. The presence of oxygen in the nitrogen is also objectionable. The fixation of nitrogen by boron is the subject of a detailed investigation by Stähler and Elbert (*Ber.*, **46**, 2060). Owing to its strong affinity for nitrogen and the fact that of all solid nitrides that of boron contains the highest per cent. of nitrogen, boron seems specially suited for the fixation of nitrogen. Boron nitride is further valuable as a refractory material, and from it may be obtained not only ammonia but also cyanides. B_2O_3 can be reduced to boron by carbon at 1200°; borax can be reduced to boron by the electric current with iron electrodes with a current yield of 12.1% theoretical. Reduction of boric acid by calcium carbide takes place at 1625°, the resultant product being from qualitative examination calcium boride, and this the most convenient method of preparing it. Borocalcite, $CaB_4O_7.4H_2O$, and carbon were heated together but even at 1700° no formation of calcium boride took place, but when nitrogen was led over the heated mass it was readily absorbed. Not only nitride but also cyanamide seems to be formed, and the reaction appears to be $CaB_4O_7 + 8C + 3N_2 = 4BN + CaCN_2 + 7CO$. No study appears to have been made as to the reversibility of this reaction. For the reaction $B_2O_3 + 3C + N_2 \rightleftharpoons 2BN + 3CO$, 1500° to 1700° is the most favorable temperature. At 1800° the heating should not be continued more than 30 minutes. Even at pressures of 40 to 70 atmospheres the amount of absorbed nitrogen was not increased (a result to be theoretically expected). The absorption of nitrogen at atmospheric pressure per gram boron is much larger when borocalcite is used than with boric acid. BN loses no weight when heated to 2200° in a graphite boat, but at 2450° it was completely destroyed, the carbide of boron being formed. These studies on nitrides are all of great value as throwing light on an extremely important industrial problem.

An investigation of the sensitiveness of the azides to the light, by Wöhler and Krupko (*Ber.*, **46**, 2045) throws some light on the photographic latent image. The action of the light on mercurous, silver, cuprous, and lead azides was studied. Especially in the first two cases no evidence of a subazide was found, though the effect of the light was in every way analogous to its action on the silver halides. The azide darkened gradually according to the amount of light, and in every case the free metal was formed with the liberation of nitrogen. Evidence is thus afforded from analogy that the latent image in photographic processes is not due to the formation of a subhalide, but to reduction to metallic silver, which forms an adsorption compound in the excess of silver halide. A basic lead azide, $PbO.PbN_6$, and a basic cupric azide of similar formula were also obtained.

A painstaking investigation of the vapor density of phosphorus has been made by Stock (*Ber.*, **45**, 3527) in a special apparatus of transparent quartz, the result showing that the molecule of phosphorus is P_4 up to 700°. The dissociation above this temperature is $P_4 \rightleftharpoons 2P_2$, and the amount of P_2 is at 800° about 1/100, at 1000° 1/10, at 1200° 1/3, all at atmospheric pressure. At one-fourth atmospheric pressure the amount of P_2 is 2/3.

A new and peculiar type of compound has been discovered by Hilpert and Herrmann (*Ber.*, 46, 2218). When molecular silver is shaken with fused $AsBr_3$ so much of the metal is taken up as corresponds to the compound Ag_3AsBr_3. That this is a chemical individual appears evident from the decomposition reactions. With aqueous ammonia or alkali, metallic silver is formed and $AsBr_3$ goes into solution; that there is a direct union between the arsenic and the bromine is evident from the action of phenylmagnesium bromide, which gives triphenyl arsine in a yield of 70%; when treated with KCN solution free arsenic is precipitated, the tendency of the silver to enter into a cyanide complex being so great that it carries the bromine with it. The compound is very stable and only at a low red heat is the arsenic sublimed in a carbon dioxide atmosphere. The constitution of the compound would seem to be  $Ag_3{>}As{<}Br_3$. The secondary valence of $AsCl_3$ and $AsBr_3$ is so strong that we have the addition products $AsCl_3.3NH_3$ and $2AsCl_3.7NH_3$. Corresponding to these the authors have prepared not only $AsBr_3.3Ag$, but also $2AsCl_3.7Ag$, $2AsCl_3.7Cu$ and $2AsBr_3.7Cu$. This investigation opens a wide field. Perhaps to the same type may belong the silver subfluoride described by Wöhler (*Z. anorg. Chem.*, 78, 239), Ag_2F, which from this standpoint could be written $Ag\cdots Ag\text{-}F$, or $AgF.Ag$; and the same may be true of the subhalides $Ca\cdots CaCl_2$, $Ca\cdots CaI_2$, and $Ca\cdots CaF_2$.

It is interesting to note that Harned (THIS JOURNAL, 35, 1078) has succeeded in preparing a columbium chloride analogous to the tantalum chloride of Chapin, and possessing similar properties. While the empiric formula is $Cb_6Cl_{14}.7H_2O$, the compound is in reality the chloride of the base $Cb_6Cl_{12}(OH)_2.8H_2O$, which is amphoteric, dissolving in HCl with the formation of the chloride $(Cb_6Cl_{12})Cl_2.7H_2O$, and in concentrated alkali with the production of (probably) $(Cb_6Cl_{12})(ONa)_2.aq$. The base also dissolves in HBr giving $(Cb_6Cl_{12})Br_2.7H_2O$.

Group VI.—A quantitative study of the oxidation of inorganic salts by ozone by Yamauchi (*Am. Chem. J.*, 49, 55) deserves notice as throwing light on the mechanism of the reaction, and possibly also on the constitution of ozone. By means of a specially constructed apparatus the author was enabled to measure the ratio between the substance oxidized and the ozone used. In the case of arsenious oxide the equation representing the reaction is $As_2O_3 + 2O_3 = As_2O_5 + 2O_2$, and also in the case of thallous nitrate, mercurous nitrate, and ammonium ferrous sulfate, each ozone molecule furnished one atom of oxygen for oxidation. In the case of stannous chloride, however, the reaction was $3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O$, all three atoms of the ozone being used for oxidation. As a matter of fact, in this case rather more stannous chloride was oxidized than indicated by the equation, which would throw some doubt upon the correctness of the equation. The first reaction between sodium thiosulfate and ozone is simply the splitting off of sulfur, $3Na_2S_2O_3 = 3Na_2SO_3 + 3S$, and in the second stage two of the three molecules of sulfite are oxidized to sulfate, $2Na_2SO_3 + 2O_3 = 2Na_2SO_4 + 2O_2$. In general it would seem that the normal reaction with ozone is the splitting off of a single atom of oxygen, which would be quite in accordance with the formula $O = O^{IV} = O$ for ozone.

In the course of investigations of the action of sulfur trioxide on salts (*Ber.*, **46**, 2513, 2525) Traube has obtained fluosulfonic acid and its salts. SO_3 is absorbed by both NaF and NH_4F, in both cases with the formation of fluosulfonates, $NaSO_3F$ and NH_4SO_3F. The fluosulfonates are stable salts, dissolving in water without decomposition to a neutral solution. So great is the tendency of these salts to form, that if potassium pyrosulfate and ammonium fluoride are dissolved in a little aqueous ammonia, alcohol will precipitate ammonium fluosulfonate from the solution. By dissolving the ammonium salt in fuming sulfuric acid and warming, the free fluosulfuric acid distils over, and by adding ammonia to the distillate the ammonium fluosulfonate is obtained. When dry sodium fluosulfonate is heated in a carbon dioxide atmosphere a gas is given off which is probably sulfuryl fluoride, SO_2F_2.

The work of Flint in splitting tellurium continues to be attacked and no one has succeeded in repeating his results. Morgan (THIS JOURNAL, **34**, 1669) has purified tellurium by repeated hydrolysis, but all his samples continued to give atomic-weight figures which lie around 127.2. Similar results have been obtained by Dudley. Uhler and Patterson (*Am. J. Sci.*, [4] **36**, 135) have made a close study of the arc spectrum of tellurium as compared with the spectrum of possible impurities, and find that that portion of Flint's tellurium which gave lower atomic weight was by no means pure, as Flint supposed, but contained traces of iron and copper. Küsnezow (*Iswestja Donschen Polyt. Inst.*, 1, ii, 380) in discussing the possibility of the atomic weight of tellurium being actually greater than that of iodine, calls attention to the fact that the increments in the atomic-weight series rise and fall alternately, 7–9–11–12–14–16–19–20–23–24, etc., and consequently the elements can be divided into two series, in each of which the atomic weight increases by the comparatively regular increment of 4, and while the atomic weight of each element in the second series is generally slightly greater than that of the corresponding element in the first series, it is not necessarily greater, and this may account for the apparently anomalous atomic weight of tellurium (and argon and cobalt?). The elements may thus be looked upon as being derived from a primitive material of two types. (A somewhat similar possibility was suggested several years ago by the reviewer.)

A rather complete study of the tellurites has been made by Lehner (THIS JOURNAL, **35**, 718) who finds that the tellurites of the alkalies exist in three types, mono, di, and tetra-tellurites, as $K_2O.TeO_2$, $K_2O.2TeO_2$, and $K_2O.4TeO_2$, all hydrated and soluble in water. The tellurites of the alkaline earths are normal and slightly soluble. Barium tellurite forms very stable double salts (solid solutions?) with barium chloride. The tellurites of the heavy metals are all insoluble in water. Tellurites oxidize by heating in the air to 440–470°, although potassium ditellurite oxidizes only to $K_2O.TeO_2.TeO_3$, and the tetratellurite does not oxidize at all.

Of the series of hydrazine salts of the types $M''Cl_2.2N_2H_4$ and $MSO_4.(N_2H_4)_2SO_4$ prepared by Curtius and Schrader in 1894, the compounds with bivalent chromium were missing. These have now been made by Traube and Passarge (*Ber.*, **46**, 1505) and prove to be unique among chromous salts in being stable in the air, indeed the dihydrazin chloride is not oxidized when suspended in water and left in contact with the air for a considerable time. This stability appears to be due in part to the slight solubility of the compounds and in part to the counteracting influence of the hydrazine. When these compounds are dissolved in acids or in ammonia they are rapidly oxidized, like other chromous salts.

Another gap has been filled the past year in the preparation of the first crystalline salts of trivalent tungsten by Olsson (*Ber.*, **46**, 566). While the white tungstic acid precipitated from tungstates by HCl goes readily over into the yellow insoluble form, it is possible by rapid working with cold HCl to carry the white acid over into a clear solution. If metallic tin is added to this clear solution it is reduced, passing through several color changes. If potassium tungstate has been used and the solution warmed with tin to 40 60°, it finally reaches a stable dark yellow-green, and on saturating this solution in the cold with HCl gas a yellow-green crystalline precipitate is obtained which is a double chloride of trivalent tungsten, of formula $K_3W_2Cl_9$, or $3KCl.2WCl_3$. From this salt by double decomposition the rubidium, cesium and thallous salts were made, and from ammonium tungstate, by a similar reduction, the ammonium chlorotungstate. All have analogous formulas and properties, insolubility in water increasing with molecular weight. The slightly soluble rubidium and cesium salts are soluble in very dilute NaOH, and a small amount of the same reagent does not precipitate solutions of chlorotungstates, but concentrated NaOH gives with these solutions a reddish brown precipitate which is insoluble in excess. In these compounds trivalent tungsten shows the same tendency to the formation of complex salts as is shown so characteristically by tungstic trioxide. By the electrolytic reduction of tungsten hexachloride in alcohol solution Fischer (*Z. anorg. Chem.*, **81**, 102, 170) has obtained a green compound which can be purified by recrystallization out of a mixture of alcohol and chloroform, and which has the formula $Cl_2W(OC_2H_5)_3$, a compound of quinquivalent tungsten. All the properties of the compound agree with this formula, but a molecular-weight determination seems to indicate a double formula, two tungsten atoms perhaps being weakly combined.

Mazzucchelli and d'Alceo (*Atti accad. Lincei, Rome*, [5] 21, ii, 620) suggest three criteria for the recognition of complex salts; the simplest is when the complex salt is less soluble than its constituents and hence separates out of solution; if the salt is more soluble than its components, especially if one of these components is but slightly soluble, one may conclude that a complex salt is present; or if in the third place there is an abnormal distribution of the components between an aqueous and a nonmiscible solvent, a similar conclusion may be drawn. If all of these criteria are wanting it is still possible that a complex salt may be present, but the stability of the complex must be very small. The authors have used these methods in testing the tendency of hexa- and quadrivalent uranium to form complex salts and addition products. Thus uranyl nitrate has no tendency to unite with mercuric cyanide, urea or thiourea; uranyl oxalate is indifferent to urea and to hexamethylenetetramine. In general, uranyl salts have no tendency to complex building with nitrogen compounds. Uranous salts with weak acids are generally basic, but a complex malonate, $Na_2U(C_3H_2O_4)_3$ was formed by the electrolytic reduction of sodium uranyl malonate. Urano-oxalic acid, $H_2U(C_2O_4)_3.8H_2O$ (oxalato-uranous acid) was readily formed and some of its salts with organic bases. Uranous sulfate, $U(SO_4)_2$ proved to be quite stable in solution.

Group VII.—An important investigation of the fluorides of the noble metals (and platinum metals) has been carried out by Ruff (*Ber.*, **46**, 920, 929). In various attempts to prepare the fluoride of platinum it was found that neither HF nor KHF_2 had any action on platinum chloride (nor on Au_2Cl_4), nor could the fluosilicate of Berzelius be obtained by evaporating the solution of PtO_2 in fluosilicic acid, hydrolysis taking place. On adding KF to a concentrated solution of $PtCl_4$, a precipitate of K_2PtCl_5-OH was obtained. The action of elementary fluorine upon the other platinum metals was tested, using boats and tubes of a mixture of 7 parts cryolite with 3 parts lithium fluoride. Rhodium was hardly attacked, even at a red heat. Palladium reacted only slowly at a red heat, becoming covered with a red-brown crystalline coating of what was probably PdF_4. Iridium also was only acted on at a low red heat. At higher temperatures heavy white fumes were formed. Ruthenium showed an action similar to that of osmium (below), but the amount of volatile compound formed was small and it was less stable than that of osmium. With osmium, fluorine reacts very readily, three different fluorides being isolated. Below 250° OsF_4 is chiefly formed, at 250° OsF_6 when the stream of fluorine is slow, and OsF_8 when the fluorine is in large excess. The study of these fluorides was carried on with great difficulty owing to several facts. Fluorine is hard to prepare, osmium is expensive, glass is more or less attacked by the fluorides, strongly if a trace of water is present, platinum tubes are opaque and the reactions cannot be seen, it is impossible to wholly exclude oxygen which contaminates everything with OsO_4, the fluorides themselves are far from stable compounds, and it is far from easy to analyze an osmium-fluorine compound or to determine the state of oxidation of the osmium. Taking these facts into consideration, the investigation was very satisfactory and deserves to be placed alongside of the work of Stock on the borides of hydrogen. OsF_4 is the result of incomplete treatment of osmium with fluorine, is soluble in water with an acid reaction, and appears to be non-volatile. OsF_6 is volatile, with a boiling point of 202–205°. It attacks glass so that its melting point could not be determined, but lies above 50°, where the action on glass begins, and below 120°. It is characterized by reacting with water, with which it gives a precipitate of OsO_2, resembling the action of SiF_4 on water. It coats anything damp, or organic, with which it may come in contact, black, in this respect resembling OsO_4. It is, however, the compound OsF_8 which presents the greatest interest, for this is the first compound containing an element which is octavalent beyond dispute (one may argue for the quadrivalence of Os and Ru in OsO_4 and RuO_4), and the only binary compound containing eight atoms of a single kind united with only one other atom, or eight atoms around a single central atom. OsF_8 is a lemon yellow, crystalline compound, with a melting point of 34.4° and boils at 47.5°. Its molecular weight corresponds to OsF_8 and the valence of the osmium is eight. It does not attack gold or platinum, but is decomposed by silver and most other metals with the formation of fluorides. Organic substances are violently attacked. It dissolves to a colorless solution in water, but obviously with decomposition, since the solution smells strongly of OsO_4. It unites with alkali fluorides extremely easily to form salt-like compounds, which decompose on treatment with NaOH with evolution of oxygen and ozone. In a platinum tube it begins to decompose at 225°.

As a source of salts of trivalent manganese, Meyer (*Z. anorg. Chem.*, **81**, 385) recommends potassium manganicyanide, which is readily prepared by drawing air through a concentrated solution of manganese carbonate in KCN. The manganicyanide can be recrystallized from a 10% KCN solution and is fairly stable in cold water. On dilution or on heating it hydrolyzes with the formation of manganic hydroxide, which is perfectly stable and which dissolves readily in acids with the formation of manganic salts. These salts with oxy-acids are intensely red or violet-red and in concentrated acid solution can be boiled without change, but are instantly hydrolyzed on dilution. Except in cold solutions HCl evolves chlorine, but HF dissolves this hydroxide to form a stable fluoride, which gives double salts, among which the red K_2MnF_5 was isolated.

Group VIII.—A paper of some importance in its bearing on the origin of pyrite deposits has appeared by Dosz (*Z. prakt. Geol.*, **20**, 453), in which a new iron disulfide, melnikowite, is described from the miocene clay in the Russian province of Samara. This mineral occurs in small, dense, dull, opaque masses, strongly magnetic, with composition FeS_2. It has an acid reaction and dissolves easily in dilute or concentrated HCl. From all its properties it is an iron disulfide gel which has become crystalloid and passes over very gradually into pyrite as a stable phase. This, Dosz considers, offers an explanation of many pyrite deposits, which are to be looked upon as syngenetic rather than epigenetic. The process of formation he describes somewhat as follows: In shallow lakes the iron is furnished as bicarbonate. This, either by hydrolytic conversion into the hydroxide with subsequent change into sulfide, or by direct precipitation as hydrosulfide, has taken up more sulfur with loss of water, forming melnikowite. The sulfur has been furnished by decomposing organic matter, and the whole course of reaction quite possibly went on under bacterial influence. Bacteria have been traced back at least to Devonian strata, and Dosz could detect fossil iron-bacteria (gallionella ferrunginea) in melnikowite. In earlier periods of geological history sulfur played a more important part in the upper portion of the earth's crust than today, and sulfurizing and desulfurizing bacteria must have had larger influence. The abundance of pyrite in round masses is much better explicable under this theory that pyrite is the stable form derived from a hydrogel.

Bellucci and Corelli (*Atti accad. Lincei, Rome* [5], **22** i, 603) have made a careful study of the well-known reduction of potassium nickel cyanide solutions by reducing agents, and come to the conclusion that univalent nickel is actually present. As a reducing agent they found sodium amalgam most satisfactory, and while, in accordance with Moore's results some years ago, the nickel-cyanide ratio seems to be 6 : 5, an examination of the valence of the nickel in the red reduced solution, by measuring the hydrogen evolved in its oxidation, and by oxidizing with iodine and with hydrogen peroxide, shows that univalent nickel is present, though no compound of univalent nickel has yet been isolated.

In the analysis of platinum ores from the urals, Holtz (*Ann. chim. Phys.*, [8] **27**, 559) has found certain anomalies which seem to point to the presence of a new metal. After precipitating the platinum from the *aqua regia* solution with sal ammoniac, the other platinum metals (and any copper) are precipitated by metallic zinc. After drying and weighing, this "black" is treated with dilute nitric acid to dissolve the palladium and copper. The other platinum metals should be insoluble, and it is just here that the anomaly occurs, for the palladium and copper come far from accounting for the loss of weight of the "black." After the removal of the palladium and copper there is left a yellow solution which gives a black foam on reduction with zinc. This black material after drying glows when heated in hydrogen and loses slightly in weight. The oxide of the metal is insoluble in all acids but dissolves in NaOH with yellow color, which does not change on acidifying with HCl. The oxide is not attacked by soda-saltpeter fusion. The metal itself is soluble in HNO_3 and HCl and its solution in the latter is not precipitated by NH_4Cl. The metal also dissolves in $KHSO_4$ fusion with red-brown color, but unlike rhodium leaves no white residue of basic sulfate on solution in water. Holtz suggests that this apparently new metal may be identical with French's canadium and Courtis' amarillium. To the reviewer, however, it seems possible that Holtz may be dealing with an impure rhodium, which sometimes itself acts in a rather anomalous manner. An interesting piece of work has been carried out by Wohler on the stability and conditions of existence of the chlorides of platinum and iridium (*Ber.*, **46**, 1577, 1591, 1720). The method used was to heat the metal, or better in the case of platinum the tetrachloride, in a current of chlorine at different temperatures, the limiting temperatures of formation and decomposition being determined by trial. $PtCl_4$ loses chlorine at 374° but takes it up again at 364°. The greenish black $PtCl_3$ is stable at 435°, losing chlorine at 440° and taking it up at 430°. The brown-green $PtCl_2$ remains unchanged in composition at 560°, though quite volatile at this temperature. If kept at 581-583° a light yellow vapor is given off and occasionally a light green residue is left with the metallic platinum in the boat, which contains both platinum and chlorine and is without much doubt the monochloride, PtCl. This has very narrow limits of stability, certainly of not more than a degree or two, at about 582°. $IrCl_4$ in a stream of chlorine loses chlorine above 200°, indeed at 100° the chlorine pressure is already greater than 1 atmosphere. $IrCl_3$ is best formed by heating iridium in chlorine at about 600°, but it is stable over the extraordinarily large range of 100-763°. At the latter temperature it loses chlorine forming $IrCl_2$, which is stable at 770° but at 780° goes over into IrCl. This also has narrow limits of existence for at 798° the metal is formed. IrCl is also more volatile than the other chlorides. The tetrachloride differs markedly in its properties from the other chlorides. It is soluble in water but the solution on evaporation in chlorine at 40° does not leave an anhydrous chloride, as chlorine is given off and the salt is more or less hydrolyzed. Gutbier (*Ber.*, **46**, 2098) has continued his work on the halogen salts of the platinum metals by preparing the hexabromo-osmates (osmeates). These cannot be satisfactorily made by the action of concentrated hydrobromic acid on the chloro-osmates, owing to the fact that the hydrobromic acid exercises a reducing action on the salts. On the other hand, by using the sodium sulfito-osmate, $2Na_2SO_3.OsO_2(SO_3)_2.5H_2O$, first prepared by Rosenheim, it was possible, by the addition of concentrated HBr, to obtain a solution of sodium hexabromo-osmate, Na_2OsBr_6. By the addition of alkali bromides to this solution the hexabromo-osmates of ammonium, potassium, rubidium and cesium were prepared, all giving fine dark red-brown octahedra. Mention should be made of the continuation of the work of Tschugajew (*Z. anorg. Chem.*, **82**, 401, 420; **83**, 8) on the complexes of platinum with dithioethers, and the extension of this work to the compounds of quadrivalent platinum with organic sulfides, and of the work of Ramberg (*Ber.*, **46**, 1696, 2353) on platinum complexes with xanthogenates and ethylthioglycolates, which is of a similar character. The work is interesting and of great theoretical importance, but is not yet sufficiently generalized for a brief abstraction. Tschugajew also shows (*Z. anorg. Chem.*, 83, 1) that dimethylglyoxime forms complex compounds with rhodium which much resemble those with cobalt but are more stable. The complex of rhodium with two molecules of the dioxime and two atoms of chlorine is a univalent negative ion, sufficiently stable for the isolation of the free acid, while the similar complex with the chlorine replaced by ammonia is a univalent kation.

The oxidizing properties of osmium tetroxide have been studied by Hofmann (*Ber.*, **45**, 3329; **46**, 1657) and it proves to have very marked catalytic properties. Its action as a carrier of atmospheric oxygen is rather slow, but more rapid under 10 atmospheres pressure and at 50–100°. 200 cc. of 40% alcohol were oxidized, chiefly to acetic acid, within three to four hours by the use of 0.01 gram OsO_4 as oxygen carrier. The catalytic action of OsO_4 is much more marked when the oxygen is furnished by chlorates. A mixture of arsenic and potassium chlorate undergoes no reaction even in the presence of dilute H_2SO_4, but if a little osmium tetroxide solution is added the temperature immediately rises and within a minute the arsenic is completely oxidized to arsenic acid with a very violent reaction. (This is valuable as a lecture experiment.) Organic substances are readily oxidized, as anthracene to anthraquinone. A paper covered with osmium dioxide hydrate is bleached in a few seconds when immersed in a neutral chlorate solution, the dioxide being oxidized to the tetroxide. It seems, from various experiments of Hofmann, that an addition compound is formed between the osmium tetroxide and the chlorate, and that this compound may act as an oxidizing agent; it must itself first unite with the substance to be oxidized, either through secondary valence or adsorption power. Hofmann finds that ruthenium tetroxide possesses a similar catalytic oxidizing power but far less strong than that of the osmium tetroxide. It seems also, from an article by Lehmann (*Arch. Pharm.*, **251**, 152), that osmium dioxide can act as a catalytic reducing agent, especially as a carrier of hydrogen to unsaturated fats. A lecture experiment is described in which 0.1 gram OsO_4 is dissolved in 10 grams olive oil and the whole heated. Then hydrogen is led into the hot oil for half an hour, and on cooling the oil solidifies. It is unfortunate that osmium is such an expensive element, as great possibilities for its industrial as well as laboratory use are indicated in these articles.

Much has been done during the past year on the radioactive elements and it looks as if their decomposition products would soon yield themselves to system and possibly even find places in the periodic system. In the near future they may come to demand a place in a review of inorganic chemistry. At present they should still be treated by themselves.

ERRATA.

HEATS OF COMBUSTION OF OCTANES.

T. W. RICHARDS AND R. H. JESSE.

Vol. 32 (1910):

P. 289, line 13, for 4.179 read 1/4.179.

P. 292, line 24, for 110.11 read 114.14.

P. 292, table, last two columns should contain the following figures in order (instead of those given): 5448, 5442, 5454, 5444, 5439 (Kilojoules); 1304, 1302, 1305, 1303, 1301 (Calories).

P. 292, second line below table, for "5247 to 5261" read "5439 to 5454."

P. 293, line 5, for "5253" read "5445."

P. 296, table, the last five numbers in the second column of figures should read "5448, 5442, 5454, 5444, 5439."

P. 296, table, the last five numbers in the last column of figures should read "5482, 5474, 5487, 5477, 5472."

P. 297, line 2, for "688" read "880;" lines 4, and 9, for "172" read "110;" line 4, for "hydrogens" read "hydrogen molecules;" line 11, for "344" read "220" and for "300" read "424."

P. 298, line 13, for "5256" read "5448;" line 14, for "5250," "5261," and "5252" read "5442," "5454," and "5444," respectively; line 15, for "5247" read "5439."

The authors are indebted to Professor W. A. Noyes of Illinois and Professor W. A. Roth, of Greifswald for the discovery of some of these errors, which are in part mere misprints and in part due to an unfathomable mistake in the assumed molecular weight of octane. Fortunately, none of the conclusions of the paper is at all affected by the mistakes, because all of the octanes were equally affected by them.

CORRECTION.

The last half of the sentence at the foot of page 89 (January number of THIS JOURNAL) instead of reading, "and the molal concentration of the H^+ ion $^2 \times 10^4$ being plotted as ordinates," should read, "and the molal concentration of the H^+ ion $\times 10^4$ being plotted as ordinates.[2]" The number ([2]) refers to a foot-note and does not mean the square of the H^+, as the reading would indicate.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

INTERPRETATIONS OF SOME STEREOCHEMICAL PROBLEMS IN TERMS OF THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCES.

I. ANOMALOUS BEHAVIOR OF CERTAIN DERIVATIVES OF BENZENE.

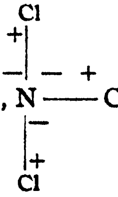
BY HARRY SHIPLEY FRY.

Received December 15, 1913.

The fundamental principles employed in various applications of the electronic conception of positive and negative valences have been presented and discussed in previous papers.[1]

The present series of papers is a further extension of the former principles in an endeavor to interpret only a few of the many stereochemical problems now confronting us and concerning which Cohen[2] tersely remarks: "It must be confessed that we are still profoundly ignorant of the change which substituents effect in the character of the molecule as a whole, the causes which determine the rules of orientation—and a host of other phenomena of a similar nature."

The particular problems to be considered in this paper relate to the anomalous behavior of certain derivatives of benzene, and the interpretations herewith offered should be regarded as an extension of those principles which are related to the electronic formula of benzene. Therefore, it will be necessary to recall briefly a few of those principles in order to present more clearly the present topics, both theoretical and experimental.

As a guiding principle, in the application of the electronic conception of positive and negative valences to the atoms of any molecule, let it be recalled that if the valence of an element is (n) the element may function in ($n + 1$) different ways. A simple illustration is found in the case of univalent chlorine ($n = 1$), which may function in ($n + 1$), *i. e.*, two different ways: positively univalent chlorine, $\overset{+}{\mathrm{Cl}}$, and negatively univalent chlorine, $\overset{-}{\mathrm{Cl}}$. Experimental evidence for the existence of positive chlorine was presented first by W. A. Noyes[3] relative to the constitution of nitrogen trichloride,  $\begin{array}{l} \mathrm{Cl} \\ +| \\ -|\;-\;+ \\ \mathrm{N}\text{——}\mathrm{Cl} \\ |- \\ |+ \\ \mathrm{Cl} \end{array}$.[4] Stieglitz[5] also postulated the existence of positively and negatively functioning chlorine from the standpoint of the interaction of chlorine and water according to the equation $\mathrm{Cl_2} + \mathrm{HOH} \rightleftarrows \mathrm{HCl} + \mathrm{HOCl}$. Employing electronic formulas, this reaction is represented as follows:

$$\mathrm{Cl}\overset{-\;+}{\text{——}}\mathrm{Cl} + \mathrm{H}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{H} \rightleftarrows \mathrm{H}\overset{+\;-}{\text{——}}\mathrm{Cl} + \mathrm{H}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{Cl}.$$

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[1] Fry, THIS JOURNAL, 30, 34 (1908); *Z. physik. Chem.*, 76, 385, 398, 591 (1911); 80, 29 (1912); 82, 665 (1913); THIS JOURNAL, 34, 664 (1912).

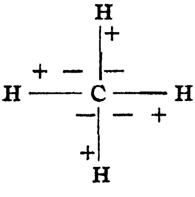
[2] "Organic Chemistry for Advanced Students," p. 293.

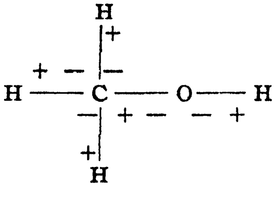
[3] THIS JOURNAL, 23, 460 (1901).

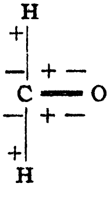
[4] *Ibid.*, 35, 767 (1913).

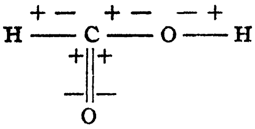
[5] *Ibid.*, 23, 796 (1901).

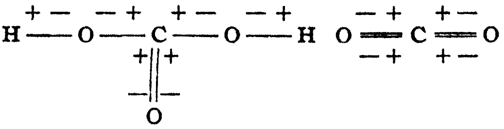
Consider now the valences of the carbon atom in the electronic formulas[1] of the typical compounds, methane, methylalcohol, formaldehyde, formic acid, carbonic acid and its anhydride, carbon dioxide. If, in these compounds, the hydrogen valences are positive and the oxygen valences negative, then the following electronic formulas result:


I.

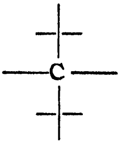

II.

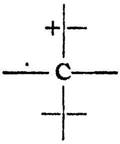

III.

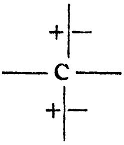

IV.

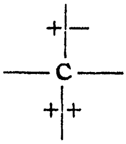

V.

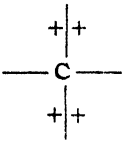
The valence (n) of the carbon atom is 4; the number of ways in which the carbon atom may function ($n + 1$) is 5. The five types (I to V) as derived from the above electronic formulas may be indicated as follows:


I.


II.


III.


IV.


V.

In terms of the electron theory the acquirement of electrons or negative valences corresponds to reduction; the loss of electrons, *i. e.*, the development of positive valences corresponds to oxidation. The above types represent the successive stages of oxidation in the transitions from methane to carbonic acid or its anhydride.

If benzene nuclei (centric formulas) are composed of the several types of carbon atoms noted above, every possible symmetrically constituted formula for benzene requires that the hydrogen atoms in positions 1, 3, and 5 are negative while the hydrogen atoms in positions 2, 4, and 6 (relatively speaking) are positive.[2] Omitting centric and double bonds, the abbreviated electronic formula of benzene is represented as follows:

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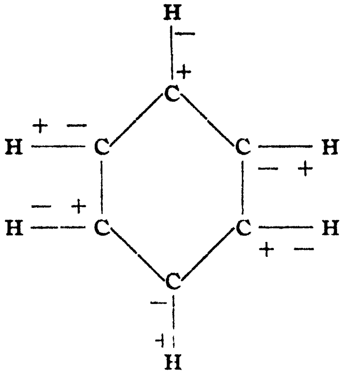
[1] Fry, *Z. physik. Chem.*, 76, 405 (1911).

[2] *Ibid.*, 76, 388 (1911).



Some of the reasons for the proposed electronic formula for benzene may be summarized briefly as follows:

(1) The Kekulé and centric formulas of benzene fail to show any structural basis for the relationships existing between ortho and para positions in contradistinction to the meta positions. The electronic formula shows that if a given hydrogen atom or substituent is negative, then those hydrogen atoms or substituents ortho and para to it are each positive while those meta to it are each negative.

(2) Collie's space formulas for benzene[1] constructed with tetrahedron models of carbon atoms shows the existence of two distinct sets of hydrogen atoms, namely, the 1,3,5-set and the 2,4,6-set. Concordantly the electronic formula for benzene presents two distinct sets of hydrogen atoms, namely, the 1,3,5-set which functions negatively in contradistinction to the 2,4,6-set which functions positively. This feature is maintained when the electronic formulas or "electromers" of benzene are in the states of dynamic equilibria presented by Collie's space formulas.[2]

(3) The existence of two sets of hydrogen atoms enabled Collie to propose a stereochemical explanation of the Crum Brown and Gibson Rule.[3] The electronic formula of benzene likewise lends itself to an interpretation of the same rule, showing how meta disubstitution derivatives are formed in some cases while ortho and para diderivatives result in others.[4]

One of the many anomalies encountered in the formation of disubstitution derivatives of benzene is the behavior of chlorobenzene and nitrobenzene when nitrated and chlorinated, respectively. Chlorobenzene when nitrated gives ortho and para chloronitrobenzenes while nitrobenzene when chlorinated yields only metachloronitrobenzene. According to principles previously developed from the Crum Brown and

[1] *J. Chem. Soc.*, 71, 1013 (1897).

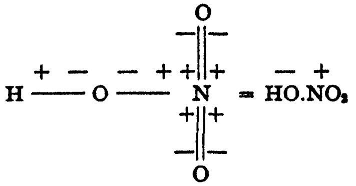
[2] Fry, *Z. physik. Chem.*, 76, 400 (1911).

[3] *J. Chem. Soc.*, 61, 366 (1892).

[4] Fry, *Z. physik. Chem.*, 76, 391 (1911).

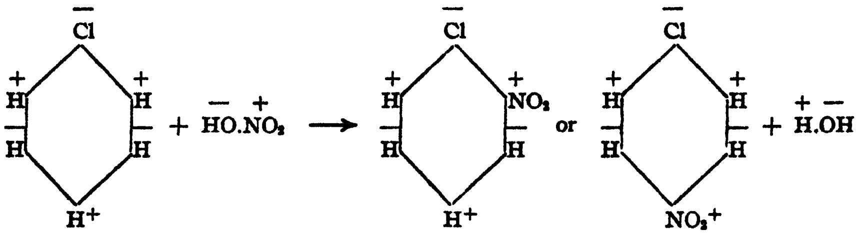
Gibson Rule, the electronic formula of chlorobenzene is $\overset{+}{C_6H_5}.\overset{-}{Cl}$ while that of nitrobenzene is $\overset{-}{C_6H_5}.\overset{+}{NO_2}$. Hypochlorous and nitric acids are represented thus:

$$\overset{+\ \ -}{H\text{——}O}\overset{-\ \ +}{\text{——}Cl} = \overset{-}{HO}.\overset{+}{Cl};$$

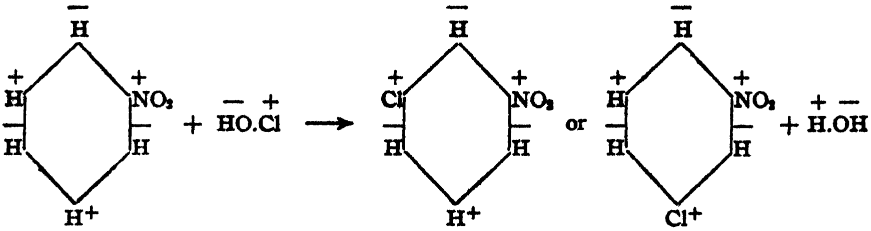


$$\overset{+\ \ -}{H\text{——}O}\overset{-\ \ +}{\text{——}N}\overset{\overset{O}{=}}{\underset{\underset{O}{=}}{}} = \overset{-}{HO}.\overset{+}{NO_2}$$

When, therefore, $\overset{+}{C_6H_5}.\overset{-}{Cl}$ is nitrated, *i. e.*, reacts with $\overset{-}{HO}.\overset{+}{NO_2}$, the positive nitro group replaces a positive hydrogen atom. Positive hydrogen atoms occupy positions ortho and para to the negative chlorine atom. Consequently the nitro radical must occupy positions either ortho or para to the chlorine atom in accordance with the following scheme:

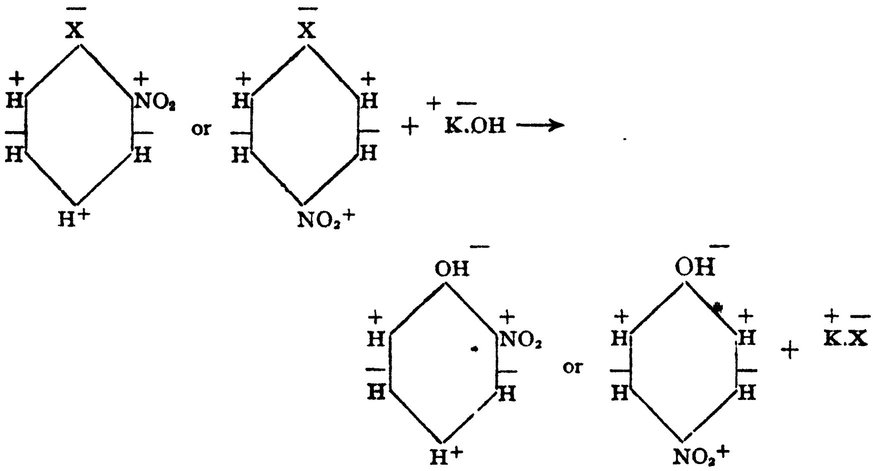


On the other hand, in the chlorination of nitrobenzene, since absolutely anhydrous chlorine does not react with anhydrous reagents, it follows that the substitution of chlorine in nitrobenzene may involve the formation of hypochlorous acid ($\overset{-}{HO}.\overset{+}{Cl}$) which in turn reacts according to the following scheme:

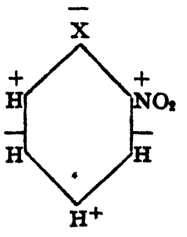


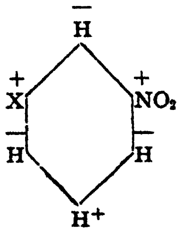
Thus when substituents are of the same sign or polarity they occupy positions which are meta to each other. If two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other. This principle may serve as the basis of a general rule for the determination of the positions of substituents in the benzene nucleus.

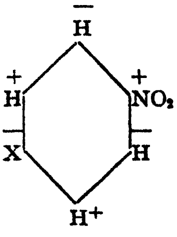
The proposed electronic formula for benzene, and the above principle of substitution applied thereto, indicate that the chlorine atom in ortho and in para chloronitrobenzene is negative while in meta chloronitrobenzene it is positive. Is there any experimental evidence to substantiate these electronic formulas of ortho, meta, and para chloronitrobenzenes? The experimental verification is presented by the apparently anomalous behavior of ortho, meta, and para, chloro- and bromonitrobenzenes when heated with potassium hydroxide. The ortho and para compounds, but not the meta, are found to exchange halogen for hydroxyl. Now the electronic formula of potassium hydroxide must be $\mathrm{K}\overset{+\quad -}{\text{——}}\mathrm{O}\overset{-\quad +}{\text{——}}\mathrm{H}$ since in its aqueous solution the ions are $\overset{+}{\mathrm{K}}$ and $\overset{-}{\mathrm{OH}}$. Interaction with ortho and para chloro- and bromonitrobenzenes results in the exchange of the halogen atoms for the *negative* hydroxyl radical. Therefore, the halogen atoms must be negative also, the reactions taking place as follows (X = Cl or Br):



On the other hand, since metachloro- and metabromonitrobenzene do not exchange their halogen atoms for the *negative* hydroxyl it follows that the halogen atoms in the meta compounds are not negative, and hence are assumed to function positively. All of these facts lead to the following electronic formulas for chloro-, bromo-, and hydroxynitrobenzenes (X = Cl, Br, or OH):

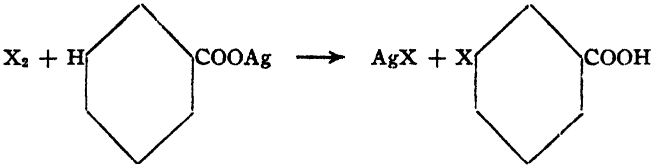






The same formulas have been derived through the application of the conception of positive and negative valences to the Brown and Gibson Rule. They are correlated to the electronic formula of benzene and afford an interpretation of the apparently anomalous behavior in the reactions just described.

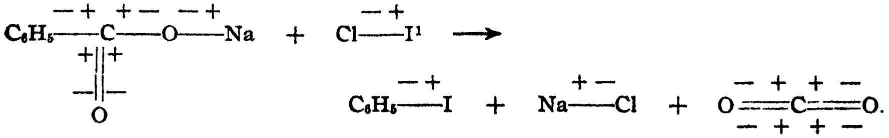
In this connection an interpretation of the action of the halogens, bromine and iodine, upon silver benzoate may be of interest. Silver benzoate reacts readily with liquid bromine, and violently with iodine at a temperature of 150°. The products are meta bromo- and meta iodobenzoic acids and silver bromide and iodide respectively: (X = Br or I)



Why does the halogen atom which enters the ring assume a position meta to the carboxyl in preference to an ortho or para position? According to the electronic conception of positive and negative valences the halogen molecule, X_2, undergoes dissociation yielding a positive and a negative halogen atom:

$$X_2 = \overset{+}{X}\text{——}\overset{-}{X} \rightleftarrows \overset{+}{X} + \overset{-}{X}$$

The electronic formula of silver benzoate requires that the carboxyl radical be positive since it is a derivative of carbonic acid in which all of the four valences of the carbon atom function positively. In other words, the carbon atom of the carboxyl radical in benzoic acid is in the same state of oxidation as is the carbon atom in carbonic acid or its anhydride, $\underset{-\;+\;\;+\;-}{\overset{-\;+\;\;+\;-}{O{=\!=}C{=\!=}O}}$. Experimental evidence substantiating this assumption is afforded by the fact that iodine chloride and sodium benzoate interact giving iodobenzene, sodium chloride and carbon dioxide according to the following equation:



$$\overset{-\;+\;\;+\;-\;\;-\;+}{C_6H_5\text{——}\underset{\substack{+\|+\\ -\|-\\ O}}{C}\text{——}O\text{——}Na} + \overset{-\;+}{Cl\text{——}I}\text{[1]} \longrightarrow \overset{-\;+}{C_6H_5\text{——}I} + \overset{+\;-}{Na\text{——}Cl} + \underset{-\;+\;\;+\;-}{\overset{-\;+\;\;+\;-}{O{=\!=}C{=\!=}O}}.$$

Since the carboxyl radical in benzoic acid is positive, the interaction

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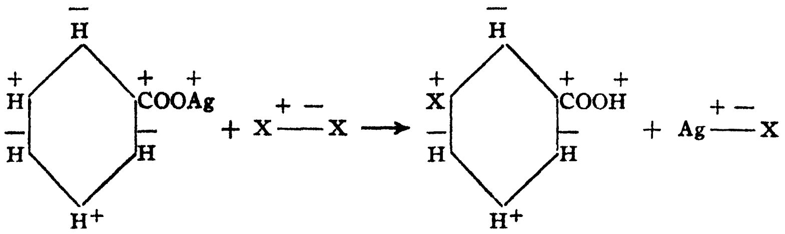
[1] The electronic formula for iodine chloride, $\overset{+\;-}{I\text{——}Cl}$, is evident from its interaction with potassium hydroxide yielding potassium chloride and potassium hypoiodite, thus:

$$2\overset{+\;-\;\;-\;+}{K\text{——}O\text{——}H} + \overset{-\;+}{Cl\text{——}I} \longrightarrow \overset{+\;-}{K\text{——}Cl} + \overset{+\;-\;\;-\;+}{K\text{——}O\text{——}I} + \overset{+\;-\;\;-\;+}{H\text{——}O\text{——}H}.$$

of the halogens, bromine and iodine, with silver benzoate must be represented by the following electronic formulas:



The positive silver must combine with negative halogen leaving the positive halogen to enter the ring. The positive hydrogen atoms of the ring occupy positions meta to the positive carboxyl group. Therefore, the entering positive halogen atom, in substituting a positive hydrogen atom, must likewise occupy a position meta to the positive carboxyl radical. This reaction substantiates the electronic formula for benzene. Furthermore, the dissociation of the halogen molecule into positive and negative parts, as indicated in the above equation, is a confirmation of the idea suggested at an earlier date by W. A. Noyes[1] that "If we suppose what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of the molecules, it would follow that elementary molecules as well may ionize into positive and negative parts."

Other stereochemical rearrangements, presented by Chattaway and Orton[2] in their study of the substituted nitrogen halides, have been interpreted in terms of positive and negative valences in a previous communication[3] further demonstrating that halogen atoms may function not only negatively but also positively.[4]

Reference may now be made to the differences in behavior of the carboxyl radicals in the benzene nucleus, some of which function negatively while others function positively. The anomalous behavior of the dihydro phthalic acids is worthy of note. Baeyer has shown that the $\Delta^{3,5}$, $\Delta^{2,4}$, and $\Delta^{2,6}$ acids when oxidized yield benzoic acid through the loss of one molecule of carbon dioxide. There has been much speculation as to why only one molecule instead of two molecules of carbon dioxide is removed from the acids in question.[1] The interpretation of this anomaly as presented in a previous paper[2] will now be briefly indicated since it is herewith to be extended to the interpretation of other anomalies manifested by certain substituted oxybenzoic acids.

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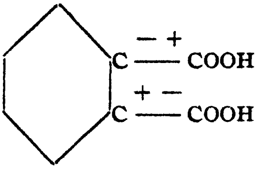
[1] THIS JOURNAL, 23, 460 (1901).

[2] *J. Chem. Soc.*, 75, 1046; *Ber.*, 32, 3572.

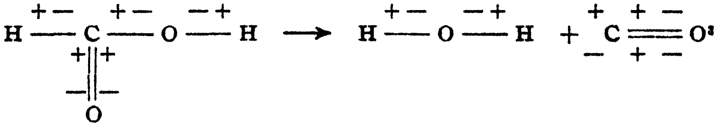
[3] Fry, THIS JOURNAL, 34, 667 (1912)

[4] The possibility of an electromer of the type $\overset{+\ -}{R.X}$ passing to an electromer of the type $\overset{-\ +}{R.X}$ is reviewed in the following paper (THIS JOURNAL). Detailed evidence of such changes is presented by L. W. Jones in the last number of the *Am. Chem. J.*, Dec., 1913.

The electronic formula of benzene requires that substituents occupying ortho positions to each other be of opposite polarity. Consequently in phthalic acid one carboxyl radical functions positively and the other negatively, thus

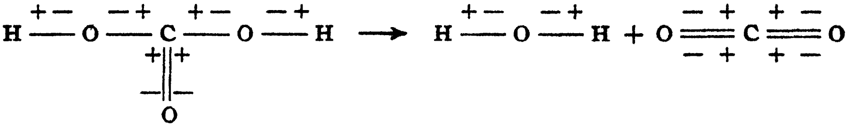


If reference be made to the electronic formulas of formic and carbonic acids, it is evident that the carboxyl radical in formic acid is negative $(\mathrm{H}\overset{+\ -}{\text{——}}\mathrm{COOH})$ while in carbonic acid it is positive, $(\mathrm{HO}\overset{-\ +}{\text{——}}\mathrm{COOH})$. Furthermore in formic acid three of the valences of the carbon atom are positive and one is negative. Accordingly formic acid on decomposition ordinarily yields carbon monoxide and water:



$$\mathrm{H}\overset{+\,-}{\text{——}}\underset{\begin{smallmatrix}+\|+\\ -\|-\\ \mathrm{O}\end{smallmatrix}}{\mathrm{C}}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\mathrm{H}\longrightarrow\mathrm{H}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\mathrm{H}+\underset{-}{\overset{+}{\mathrm{C}}}\underset{+\,-}{\overset{+\,-}{=\!=\!=}}\mathrm{O}^{3}$$

On the other hand, in carbonic acid and its anhydride each of the four valences is positive. Accordingly carbonic acid on decomposition yields water and carbon dioxide:



$$\mathrm{H}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\underset{\begin{smallmatrix}+\|+\\ -\|-\\ \mathrm{O}\end{smallmatrix}}{\mathrm{C}}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\mathrm{H}\longrightarrow\mathrm{H}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\mathrm{H}+\mathrm{O}\underset{-\,+}{\overset{-\,+}{=\!=\!=}}\mathrm{C}\underset{+\,-}{\overset{+\,-}{=\!=\!=}}\mathrm{O}$$

From the above it is evident that a carboxyl radical which is negative corresponds to the stage of oxidation represented by the carbon atom in formic acid, which does not lose carbon dioxide. On the other hand a carboxyl radical which is positive corresponds to the stage of oxidation represented by the carbon atom in carbonic acid, which very readily loses

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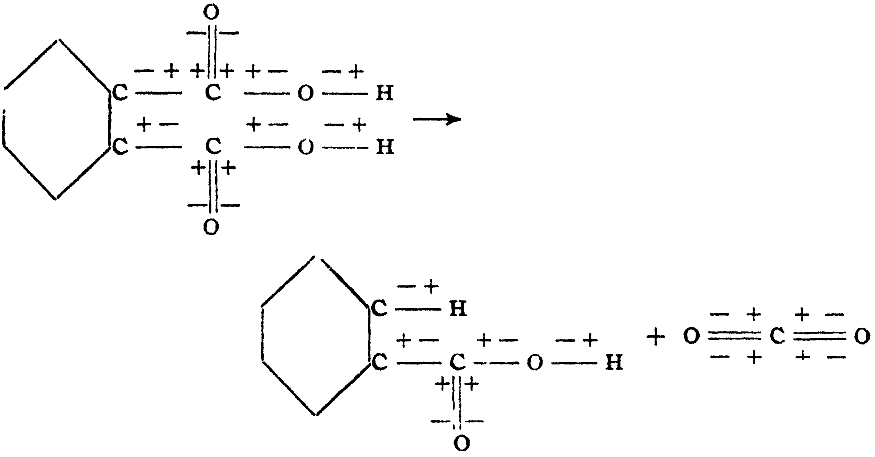
[1] Baeyer, *Ann.*, 269, 178 (1892); Brühl, *J. prakt. Chem.*, [2] 49, 229 (1894); Cohen, "Organic Chemistry" (Longmans, Green & Co.), 1907, p. 461.

[2] Fry, THIS JOURNAL, 34, 671 (1912).

[3] The free positive and the free negative valence of the carbon atom in carbon monoxide become neutral. In other words, carbon in carbon monoxide is divalent:

$$\underset{-}{\overset{+}{\mathrm{C}}}\underset{+\,-}{\overset{+\,-}{=\!=\!=}}\mathrm{O}\longrightarrow\mathrm{C}\underset{+\,-}{\overset{+\,-}{=\!=\!=}}\mathrm{O}$$

carbon dioxide. Therefore, dihydro phthalic acid, which embodies a negative carboxyl radical and a positive carboxyl radical, loses only one molecule of carbon dioxide, a result of the decomposition of the positive carboxyl radical as indicated in the following scheme:



This explanation may now be extended to the interpretation of many other anomalous phenomena involving the liberation of carbon dioxide from various substituted benzoic acids.

Cazeneuve[1] in a study of the decomposition of various hydroxybenzoic acids found that some of them readily lose carbon dioxide when heated with water or aniline, while others were quite stable. For instance, orthohydroxybenzoic acid (salicylic acid) when heated with aniline to 240° in a sealed tube gave phenol and carbon dioxide. Parahydroxybenzoic acid likewise gave carbon dioxide but the meta acid suffered no change. The instability of the ortho and the para acids and the stability of the meta acid may be interpreted in terms of the electronic formula of benzene and the polarity of the carboxyl radicals. These radicals in ortho and parahydroxybenzoic acids must function positively, *i. e.*, they correspond to the state of oxidation represented by carbonic acid and therefore may yield carbon dioxide. Furthermore, if the hydroxyl radical in the hydroxy benzoic acids is negative, then the electronic formulas for the ortho- and parahydroxybenzoic acids require that the carboxyl radicals be positive, while the carboxyl radical in the meta acid must be negative. The metacarboxyl radical being negative corresponds to the state of oxidation of formic acid and, therefore, does not lose carbon dioxide. The correlation of these phenomena with the conception of positive and negative valences is expressed in the following formulas for ortho-, para- and metahydroxybenzoic acids:

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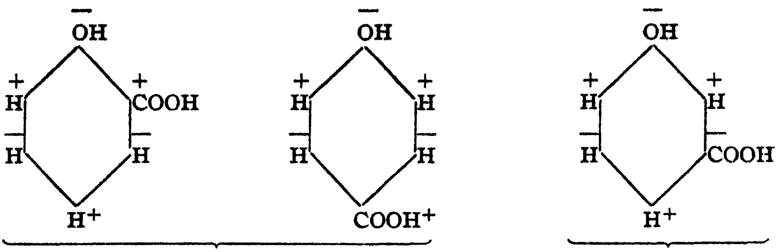
[1] *Bull. soc. chim.*, [3] 15, 7 (1896).



(unstable: lose carbon dioxide) (stable)

From the above, a general conclusion may be drawn, namely, that *a carboxyl radical either ortho or para to a negative hydroxyl radical is positive and, therefore, unstable, yielding carbon dioxide when heated with water or aniline.* On the other hand, *a carboxyl radical meta to a negative hydroxyl radical is also negative and, therefore, stable, not yielding carbon dioxide when heated with water or aniline.*

The above conclusion receives remarkable confirmation by the recent and numerous experiments of Hemmelmayr[1] in an extensive research "Concerning the influence of the nature and position of substituents upon the stability of the carboxyl radical in the substituted benzoic acids." Cazeneuve estimated the relative stability of the carboxyl radicals by comparing temperatures at which different compounds eliminated carbon dioxide. Hemmelmayr's method is more comprehensive, in that he heated weighed quantities of various acids with either 50 cc. of water or 50 cc. of aniline and estimated quantitatively the amounts of carbon dioxide liberated. In this manner he experimented with thirty-nine differently substituted hydroxybenzoic acids. Their behavior in general conformed to the rule indicated above. In other words, an examination of the formula showed that every acid which contained a carboxyl radical either ortho or para to an hydroxyl radical yielded carbon dioxide. On the other hand, those acids in which the carboxyl group was neither ortho nor para but only meta to an hydroxyl radical did not yield carbon dioxide. Thirty-five of the thirty-nine variously substituted hydroxybenzoic acids conformed to this generalization. Among thirteen mono-, di-, and trihydroxybenzoic acids there was not one exception. Hence it must be concluded that the electronic formula of benzene and the conception of positively and negatively functioning carboxyl radicals afford an interpretation of the anomalous behavior of numerous and differently substituted hydroxybenzoic acids, some of which lose carbon dioxide while others do not.

While it is thus evident that positively functioning carboxyl radicals lose carbon dioxide when heated with water or aniline, nothing has been found in the literature which would indicate or explain the mechanism of these reactions.

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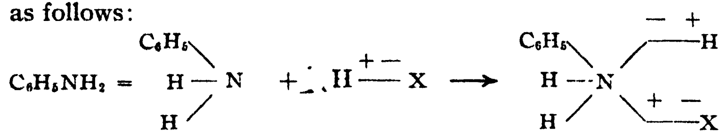
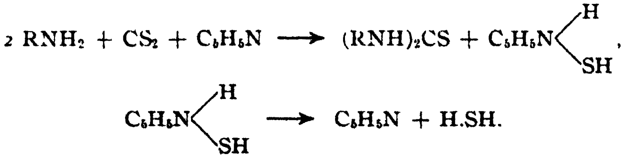
[1] *Monatsh.*, 34, 365 (1913).

In attempting to explain the action of water or aniline it should be noted that each of these reagents, which effect the elimination of carbon dioxide contains an unsaturated atom, *i. e.*, oxygen may increase its valence from two to four while nitrogen in aniline and other amines (or ammonia) may increase its valence from three to five. For instance, the combination of aniline with hydrogen halide ($H \overset{+\ \ -}{\text{——}} X$) may be represented as follows:



Since Hemmelmayr has found that amines other than aniline effect the elimination of carbon dioxide it is advisable now to limit this explanation to the unsaturated state of the nitrogen atom in amines.

In a recent paper[1] I have shown that the unsaturated nitrogen atom in the amine, pyridine, lends itself to the elimination of hydrogen sulfide in a new reaction for the preparation of thiocarbanilides, according to the equations:

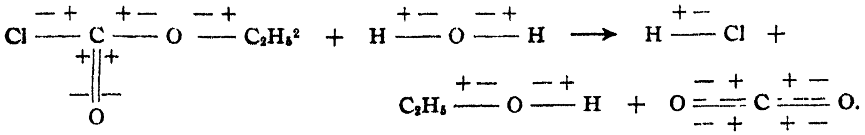


$$2\,RNH_2 + CS_2 + C_5H_5N \longrightarrow (RNH)_2CS + C_5H_5N\begin{matrix}/H\\ \backslash SH\end{matrix},$$

$$C_5H_5N\begin{matrix}/H\\ \backslash SH\end{matrix} \longrightarrow C_5H_5N + H.SH.$$

In other words pyridine combines with the elements of hydrogen sulfide forming the unstable pyridinium sulfide which, decomposing, regenerates the original pyridine and eliminates hydrogen sulfide. Analogously it may be assumed that an unstable addition compound of an amine and the oxybenzoic acid is formed which, decomposing, regenerates the amine and liberates carbon dioxide.

The validity of this assumption was put to an experimental test by employing pyridine as the amine and chlorocarbonic ethylester as an analogue of an hydroxybenzoic acid. The possibility of the elimination of carbon dioxide from chlorocarbonic ethylester is warranted, since all of the valences of its carbon atom are positive and so correspond to the state of oxidation of the carbon atom in carbonic acid and carbon dioxide. This follows from its interaction with water:



$$Cl \overset{-\ +}{\text{——}} \underset{O}{\underset{-\|-}{\underset{+\|+}{C}}} \overset{+\ -}{\text{——}} O \overset{-\ +}{\text{——}} C_2H_5{}^2 + H \overset{+\ -}{\text{——}} O \overset{-\ +}{\text{——}} H \longrightarrow H \overset{+\ -}{\text{——}} Cl + C_2H_5 \overset{+\ -}{\text{——}} O \overset{-\ +}{\text{——}} H + O \underset{-\ +}{\overset{-\ +}{=\!=}} C \underset{+\ -}{\overset{+\ -}{=\!=}} O.$$

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[1] This Journal, 35, 1539 (1913).

[2] Chlorocarbonic ethylester is very frequently but incorrectly called "chloroformic ethylester" which implies that it is a derivative of formic acid. If such were

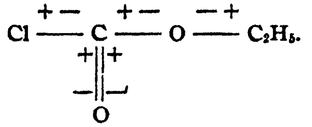
When chlorocarbonic ethylester is dissolved in an anhydrous solvent (carbon tetrachloride, benzene, or toluene) the addition of a like solution of pyridine yields at once an extremely unstable addition-compound (white solid, not yet isolated) which spontaneously decomposes, liberating carbon dioxide and ethyl chloride. The following experiments were performed in order to determine quantitatively the extent of the decomposition of various amounts of chlorocarbonic ethylester by a fixed amount of pyridine.

3.95 grams of pyridine ($^1/_{20}$ mole) were dissolved in 25 cc. of absolute toluene, contained in a 200 cc. round bottomed flask suspended in a water bath. The flask was securely fitted to a dropping funnel (for the introduction of the chlorocarbonic ethylester) and to a long, upright spiral condenser. The upper end of the condenser was connected by glass tubing to a gas washing bottle containing toluene which was kept at a constant temperature of 0° (for the absorption of ethyl chloride) and saturated with carbon dioxide. The wash-bottle was in turn connected to U-tubes filled with soda-lime and accurately weighed for the absorption of carbon dioxide liberated in the reaction.

2.71 grams ($^1/_{40}$ mole) of chlorocarbonic ethylester dissolved in 10 cc. of toluene were admitted to the flask by way of the dropping funnel. The white, flaky solid which was formed immediately decomposed with such vigor that it became necessary to immerse the flask in cold water, and thereby control the rate of the elimination of carbon dioxide. The last traces of carbon dioxide had to be driven over by heating the reaction mixture and then drawing air through the entire apparatus. The increase in weight of the U-tubes due to the absorption of carbon dioxide was 0.9720 gram.

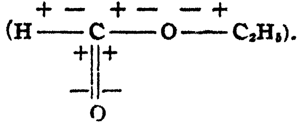
The above operation (addition of $^1/_{40}$ mole chlorocarbonic ethylester and its subsequent decomposition) was carried out three times in succession, thereby bringing into reaction $^1/_{40}$, $^2/_{40}$, and $^3/_{40}$ moles of the ester

the case then its carbon atom must possess three positive valences and one negative valence in order that it correctly correspond to the state of oxidation of the carbon atom in formic acid. Its electronic formula would then be as follows:



$$\mathrm{Cl}\overset{+\;-}{\text{——}}\underset{\substack{+\Vert+\\ -\Vert-\\ \mathrm{O}}}{\mathrm{C}}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{C_2H_5}.$$

This "electromer" if hydrolyzed could not yield carbon dioxide directly. The products would be hypochlorous acid $(\mathrm{H}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{Cl})$ and ethyl formate

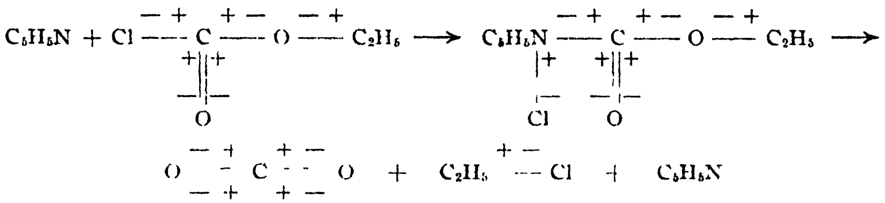


$$(\mathrm{H}\overset{+\;-}{\text{——}}\underset{\substack{+\Vert+\\ -\Vert-\\ \mathrm{O}}}{\mathrm{C}}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{C_2H_5}).$$

with a fixed quantity ($^1/_{20}$ mole) of pyridine. Each addition was accompanied by an energetic liberation of carbon dioxide and ethyl chloride. The following table presents the molecular ratios of the interacting substances, the quantities employed, the amounts of carbon dioxide evolved and the corresponding percentages of the theoretical yields of carbon dioxide based upon the ratio $ClCO_2C_2H_5 : CO_2$:

Molecular ratios.	C_5H_5N. (Grams)	$ClCO_2C_2H_5$. (Grams)	CO_2. (Grams.)	Per cent. of theory.
2 C_5H_5N : 1 $ClCO_2C_2H_5$........	3.95	2.71	0.9720	88.36
2 C_5H_5N : 2 $ClCO_2C_2H_5$........	3.95	5.42	1 8960	86.18
2 C_5H_5N : 3 $ClCO_2C_2H_5$........	3.95	8.13	2.7305	82 74

The reaction mixture in the flask still contained pyridine which effected the decomposition of additional quantities of chlorocarbonic ethylester. Hence it must be concluded that the pyridine acts as a catalytic agent in effecting the elimination of carbon dioxide from the ester through the intermediate formation of an unstable addition compound. The reactions involved may be represented by the following equations:

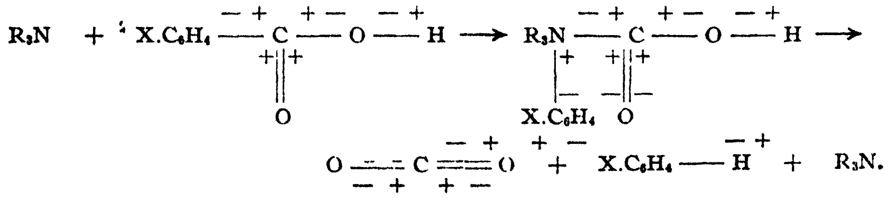


$$\mathrm{C_5H_5N} + \mathrm{Cl} \overset{-\ +}{\text{—}} \underset{\substack{+\|+\\ -\|-\\ \mathrm{O}}}{\mathrm{C}} \overset{+\ -}{\text{—}} \mathrm{O} \overset{-\ +}{\text{—}} \mathrm{C_2H_5} \longrightarrow \underset{\substack{|+\\ |-\\ \mathrm{Cl}}}{\mathrm{C_5H_5N}} \overset{-\ +}{\text{—}} \underset{\substack{+\|+\\ -\|-\\ \mathrm{O}}}{\mathrm{C}} \overset{+\ -}{\text{—}} \mathrm{O} \overset{-\ +}{\text{—}} \mathrm{C_2H_5} \longrightarrow$$

$$\mathrm{O} \overset{-\ +}{\underset{-\ +}{=}} \mathrm{C} \overset{+\ -}{\underset{+\ -}{=}} \mathrm{O} + \mathrm{C_2H_5} \overset{+\ -}{\text{—}} \mathrm{Cl} + \mathrm{C_5H_5N}$$

I have found that amines, other than pyridine, also effect the elimination of carbon dioxide from chlorocarbonic methyl-, ethyl- and propylesters. Hemmelmayr has found that amines other than aniline effect the elimination of carbon dioxide from various hydroxybenzoic acids in which the carboxyl radicals have been shown to function positively. Therefore, equations perfectly analogous to those above may represent the action of an amine of the general formula R_3N upon an hydroxybenzoic acid (or any other substituted benzoic acid in which the carboxyl radical is positive) as follows:[1]

(R = alkyl, aryl, or H; X = OH or other substituent):



$$\mathrm{R_3N} + \mathrm{X.C_6H_4} \overset{-\ +}{\text{—}} \underset{\substack{+\|+\\ \|\\ \mathrm{O}}}{\mathrm{C}} \overset{+\ -}{\text{—}} \mathrm{O} \overset{-\ +}{\text{—}} \mathrm{H} \longrightarrow \underset{\substack{|+\\ |-\\ \mathrm{X.C_6H_4}}}{\mathrm{R_3N}} \overset{-\ +}{\text{—}} \underset{\substack{+\|+\\ -\|-\\ \mathrm{O}}}{\mathrm{C}} \overset{+\ -}{\text{—}} \mathrm{O} \overset{-\ +}{\text{—}} \mathrm{H} \longrightarrow$$

$$\mathrm{O} \overset{-\ +}{\underset{-\ +}{=}} \mathrm{C} \overset{+\ -}{\underset{+\ -}{=}} \mathrm{O} + \mathrm{X.C_6H_4} \overset{-\ +}{\text{—}} \mathrm{H} + \mathrm{R_3N}.$$

The formation of an intermediate unstable compound of the amine and the acid depends upon an increase in the valence of the nitrogen from three to five. Similarly, the action of water in effecting the elimination of carbon dioxide would depend upon the formation of an unstable oxonium compound through an increase in the valence of the oxygen atom from two to four as indicated in the following equations, which are perfectly analogous to those above:

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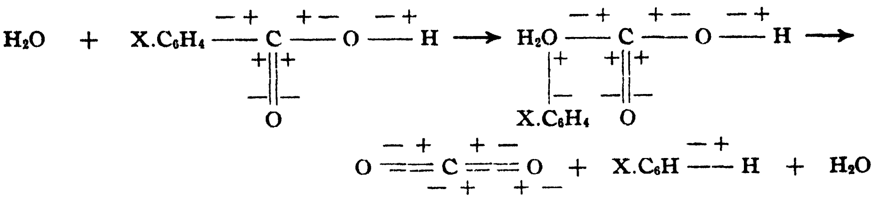
[1] Equations showing the formation of the amine salts of the acids have been omitted as they are not essential to the principal changes involved.



$$H_2O + X.C_6H_4 \overset{-\ +}{\text{——}} \underset{\underset{O}{\overset{+\|+}{\underset{-\|-}{}}}}{C} \overset{+\ -}{\text{——}} O \overset{-\ +}{\text{——}} H \longrightarrow \underset{\underset{X.C_6H_4}{\overset{|+}{\underset{|-}{}}}}{H_2O} \overset{-\ +}{\text{——}} \underset{\underset{O}{\overset{+\|+}{\underset{-\|-}{}}}}{C} \overset{+\ -}{\text{——}} O \overset{-\ +}{\text{——}} H \longrightarrow$$

$$O \underset{-\ +}{\overset{-\ +}{=\!=}} C \underset{+\ -}{\overset{+\ -}{=\!=}} O + X.C_6H \overset{-\ +}{\text{——}} H + H_2O.$$

Thus the electronic conception of positive and negative valences not only indicates the nature of the radicals which, through the action of amines or water, lose carbon dioxide but it also affords a possible interpretation of the way in which the reactions proceed. The theoretical deductions are based upon experimental facts and data afforded by the analogous action of pyridine upon chlorocarbonic ethylester.

In conclusion it may be remarked that the electronic conception of positive and negative valences and the electronic formula of benzene, afford explanations of certain anomalous properties and reactions which are generally classed as stereochemical problems. The possibility of interpreting some of these properties and reactions indicates that they are not necessarily anomalous or irregular. Hence it is hoped that a further extension of the principles and methods herewith presented may lead to the interpretation and solution of other problems.

The following article may be regarded as a continuation of the present paper, but only in so far as it relates to the electronic formula of benzene, which involves the question of the existence of negatively functioning hydrogen.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

POSITIVE AND NEGATIVE HYDROGEN, THE ELECTRONIC FORMULA OF BENZENE, AND THE NASCENT STATE.

BY HARRY SHIPLEY FRY

Received December 15, 1913.

That a univalent atom, chlorine for example, may function either positively or negatively has been conclusively demonstrated from several different standpoints.[1] The other halogens, bromine and iodine, also have been shown to dissociate into positive and negative parts in their interactions with silver benzoate.[1] Accordingly, if X_2 represent molecular halogen, dissociation from the standpoint of the electronic conception of positive and negative valences is represented thus:

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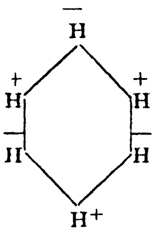
[1] W. A. Noyes, THIS JOURNAL, 23, 460 (1901); 35, 767 (1913); Stieglitz, *Ibid.*, 23, 796 (1901); Walden, *Z. physik. Chem.*, 43, 385 (1903); Fry, *Ibid.*, 76, 387, 395 (1911).

$$X_2 = X\overset{+\ -}{\text{——}}X \rightleftarrows \overset{+}{X} + \overset{-}{X}.$$

From the same standpoint, one may assume that molecular hydrogen dissociates into positive and negative hydrogen. While the existence of positive hydrogen (hydrogen ion, $\overset{+}{H}$) is indisputable the question of the existence of negative hydrogen is open to discussion.

In previous papers it has been shown that the occurrence of three positive and three negative hydrogen atoms in the electronic formula of benzene



is a necessary consequence of the application of the electronic conception of positive and negative valences to the constituent atoms of the benzene molecule. Hence, the purpose of the present paper is threefold: (1) To offer theoretical arguments for, and experimental evidence of the existence of negative hydrogen; (2) to consider the facts which require the assumption of the existence of positively and negatively functioning hydrogen atoms in the benzene nucleus; and (3) to propose a definition of the so-called "nascent state."

A rigid application of the conception of positive and negative valences to the molecular formulas of hydrogen and chlorine has led to conclusions which have not as yet been completely verified by experiment. For instance the molecular formulas of these gases and their chemical combination, preceded by dissociation, may be represented as follows:

$$\begin{array}{lcccc}
C_2 = H\overset{+\ -}{\text{——}}H & \rightleftarrows & \overset{+}{H} & + & \overset{-}{H} \\
Cl_2 = Cl\overset{-\ +}{\text{——}}Cl & \rightleftarrows & \overset{-}{Cl} & + & \overset{+}{Cl} \\
 & & \downarrow\uparrow & & \downarrow\uparrow \\
 & & H\overset{+\ -}{\text{——}}Cl & & H\overset{-\ +}{\text{——}}Cl
\end{array}$$

Thus, when two or more types of a structural formula are possible I have termed them, for the sake of reference, "electronic isomers" or, more briefly, "electromers."[2] In order to account for the existence of only one electromer, when theoretically two (or more) are possible, the following assumptions have been made: One electromer may revert to another through the transposition of electrons as indicated in the scheme: $\mathrm{H}\overset{+\ -}{\text{——}}\mathrm{Cl} \rightleftarrows \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} \rightleftarrows \overset{+}{\mathrm{H}} + \ominus + \mathrm{Cl} \rightleftarrows \mathrm{H} + \mathrm{Cl} \rightleftarrows \mathrm{H} + \ominus + \overset{+}{\mathrm{Cl}} \rightleftarrows \overset{-}{\mathrm{H}} + \overset{+}{\mathrm{Cl}} \rightleftarrows \mathrm{H}\overset{-\ +}{\text{——}}\mathrm{Cl}$; or the one electromer may be the predominating or sole type, depending upon certain physical conditions. For example an aqueous solution of hydrogen chloride yields positive hydrogen and negative chlorine ions. Therefore, the dissociating molecules are presumably of the type $\mathrm{H}\overset{+\ -}{\text{——}}\mathrm{Cl}$.

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[1] Fry, preceding paper.

[2] Fry, *Z. physik. Chem.*, 76, 387 (1911).

The assumed existence of two types of hydrogen chloride, $\overset{+}{\mathrm{H}}.\overset{-}{\mathrm{Cl}}$ and $\overset{-}{\mathrm{H}}.\overset{+}{\mathrm{Cl}}$, is paralleled by the two possible types of chlorobenzene, $\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{Cl}}$ and $\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{Cl}}$, which in turn may be regarded as derivatives of $\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{H}}$ and $\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}}$, respectively. Notwithstanding the fact that only one monochlorobenzene is known, it has been shown in the preceding paper that the benzene nucleus is united to negative chlorine in ortho and in para chloronitrobenzenes $(\mathrm{NO_2}\overset{+\ -}{\text{——}}\mathrm{C_6H_4}\overset{+\ -}{\text{——}}\mathrm{Cl})$, and to positive chlorine in metachloronitrobenzene $(\mathrm{NO_2}\overset{+\ -}{\text{——}}\mathrm{C_6H_4}\overset{-\ +}{\text{——}}\mathrm{Cl})$. Why then are there not two monochlorobenzenes? One is compelled to assume, either that the one electromer is unstable (under ordinary physical conditions) and that it reverts to the known stable electromer through the transposition of electrons, thus,

$$\mathrm{C_6H_5}\overset{-\ +}{\text{——}}\mathrm{Cl} \longrightarrow \mathrm{C_6H_5Cl} \longrightarrow \mathrm{C_6H_5}\overset{+\ -}{\text{——}}\mathrm{Cl};$$

or that monochlorobenzene is an equilibrium mixture of two tautomeric electromers, thus,

$$\mathrm{C_6H_5}\overset{-\ +}{\text{——}}\mathrm{Cl} \rightleftarrows \mathrm{C_6H_5}\overset{+\ -}{\text{——}}\mathrm{Cl}.$$

This latter assumption could be verified if it were possible to hydrolyze chlorobenzene and thereby obtain two different products, namely, phenol and benzene, according to the following equations, (1) and (2), respectively:

$$(1)\quad \overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{OH}} \longrightarrow \overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{Cl}}$$

$$(2)\quad \overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{Cl}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{OH}} \longrightarrow \overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}} + \overset{-}{\mathrm{HO}}.\overset{+}{\mathrm{Cl}}$$

But, as a matter of fact, monochlorobenzene does not undergo hydrolysis either by acids or bases. In other words, it has been impossible so far to prove directly whether the chlorine atom in monochlorobenzene is positive or negative. This, however, is not the case with all monosubstituted derivatives of benzene. For instance, in the preceding paper, it has been shown that the carboxyl radical in benzoic acid is positive. Furthermore, the (SO_3H) radical in phenylsulfonic acid may function either positively or negatively. This follows from the fact that phenylsulfonic acid on hydrolysis *in alkaline solution*[1] yields phenol and sulfurous acid while *in acid solution* or with superheated steam the products are benzene and sulfuric acid. The equations for these reactions (perfectly analogous to equations (1) and (2) above), are as follows:

$$(1)\quad \overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{SO_3H}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{OH}} \longrightarrow \overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{SO_3H}}$$

$$(2)\quad \overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{SO_3H}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{OH}} \longrightarrow \overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}} + \overset{-}{\mathrm{HO}}.\overset{+}{\mathrm{SO_3H}}.$$

L. W. Jones was the first to consider the hydrolysis of phenylsulfonic acid from an electronic standpoint, regarding the transfer of electrons between the carbon and sulfur atoms as an intramolecular oxidation or reduction.[2] Subsequently, Bray and Branch[3] interpreted this behavior of phenylsulfonic acid as an example of tautomerism:

$$\mathrm{C_6H_5}\overset{+\,-}{\text{——}}\mathrm{SO_3H} \rightleftarrows \mathrm{C_6H_5}\overset{-\,+}{\text{——}}\mathrm{SO_3H}.$$

The experimental facts, interpreted from either of the above viewpoints, lead to the conclusion that the electromers of phenylsulfonic acid may be regarded as derivatives of $\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{H}}$ and $\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}}$, respectively. Furthermore the hydroxybenzoic acids, ortho and para, have been shown to contain positive carboxyl radicals, while the metahydroxybenzoic acid contains a negative carboxyl radical. These compounds may likewise be regarded as derivatives of $\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}}$ and $\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{H}}$, respectively.

The formulas of the various derivatives of benzene heretofore considered may now be tabulated in two columns. Those in the first column are to be regarded as derivatives of $\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}}$, those in the second column as derivatives of $\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{H}}$.

$\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}}$	$\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{H}}$
$(\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{Cl}})$?	$(\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{Cl}})$?
$\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{SO_3H}}$*	$\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{SO_3H}}$*
meta-$(\mathrm{NO_2})\overset{-}{\mathrm{C_6H_4}}.\overset{+}{\mathrm{Cl}}$*	ortho-$(\mathrm{NO_2})\overset{+}{\mathrm{C_6H_4}}.\overset{-}{\mathrm{Cl}}$*
	para-$(\mathrm{NO_2})\overset{+}{\mathrm{C_6H_4}}.\overset{-}{\mathrm{Cl}}$*
ortho-$(\mathrm{HO})\overset{-}{\mathrm{C_6H_4}}.\overset{+}{\mathrm{COOH}}$*	meta-$(\mathrm{HO})\overset{+}{\mathrm{C_6H_4}}.\overset{-}{\mathrm{COOH}}$*
para-$(\mathrm{HO})\overset{-}{\mathrm{C_6H_4}}.\overset{+}{\mathrm{COOH}}$*	

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[1] It is noteworthy that phenol is formed in the presence of negative hydroxyl ion while the hydrocarbon, benzene, is formed in the presence of positive hydrogen ion. This feature will be considered more fully in a subsequent paper.

[2] Jones, *Am. Chem. J.*, 48, 26 (1912).

[3] THIS JOURNAL, 35, 1445 (1913).

It should be noted that the polarity of the radicals followed by an asterisk has been confirmed either directly or indirectly by experimental observations described in previous papers, from which it is evident that certain substituents in the benzene nucleus function sometimes positively, sometimes negatively. It may then be concluded that those atoms or radicals which function positively have substituted positive hydrogen atoms of the nucleus. On the other hand, those atoms or radicals which function negatively have substituted negative hydrogen atoms of the nucleus. This, of course, is only an indirect proof of the existence of positive and negative hydrogen atoms in the benzene nucleus. In like manner we speak of the existence of carbonic and sulfurous acids when as a matter of fact chiefly their derivatives, that is to say their substitution products, are known. A direct proof of the existence of negative hydrogen will be presented after some theoretical arguments have been considered.

It has been observed that only one electromer of hydrogen chloride is known, namely, $(\overset{+}{H}\text{——}\overset{-}{Cl})$, since its aqueous solution yields positive hydrogen and negative chlorine ions. It has also been shown on theoretical grounds that this fact does not preclude the possible existence of negative hydrogen and positive chlorine ions in an aqueous solution.[1] For instance, during the electrolysis of hydrochloric acid, negative hydrogen may result by cathodic reduction, and positive chlorine ions arise by anodic oxidation: A hydrogen atom carrying a unit positive charge may lose it on contact with the cathode; $\overset{+}{H} + \ominus \longrightarrow H$. The resulting neutral atom immediately acquiring a negative charge becomes a negative hydrogen ion; $H + \ominus \longrightarrow \overset{-}{H}$, which is then immediately repelled from the cathode to combine with one of the approaching positive hydrogen ions, thus forming a molecule of hydrogen; $\overset{-}{H} + \overset{+}{H} \longrightarrow \overset{+}{H}\text{——}\overset{-}{H} = H_2$. An analogous and simultaneous process may take place at the anode:

$$\overset{-}{Cl} + \oplus \longrightarrow Cl;\quad Cl + \oplus \longrightarrow \overset{+}{Cl};\quad \overset{+}{Cl} + \overset{-}{Cl} \longrightarrow \overset{+}{Cl}\text{——}\overset{-}{Cl} = Cl_2.$$

Are there any facts to warrant the assumption of the existence of positive chlorine ions at the anode? The existence of positive chlorine ions is substantiated by the apparently anomalous facts, that on electrolysis concentrated solutions of hydrochloric acid yield equal volumes of hydrogen and chlorine while very dilute solutions yield hydrogen at the cathode, but no free chlorine at the anode. Instead an equivalent amount of oxygen is evolved. Ostwald[2] states that "This is due to the fact that the water is decomposed by the chlorine with the formation of hydrogen chloride and oxygen according to the equation $2\ H_2O + 2\ Cl_2 = 4\ HCl +$

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[1] Fry, *Z. physik. Chem.*, **76**, 387 (1911).

[2] "Principles of Inorganic Chemistry," p. 195 (1902).

O_2. This process, it is true, takes place with measurable velocity only in light; we may, however, assume here, as in similar cases, that the process takes place without light, only very slowly." This explanation may be modified and extended since the liberation of oxygen from solutions of chlorine in water is due to the decomposition of the intermediately formed hypochlorous acid according to the generally accepted equations:

$$Cl_2 + HOH \rightleftarrows HCl + HOCl; \quad 2HOCl \longrightarrow 2HCl + O_2.$$

To admit the existence of hypochlorous acid is to admit the existence of positive chlorine, $(\overset{-}{HO}.\overset{+}{Cl})$. The decomposition of water by chlorine may be regarded as an oxidation of the hydroxyl ion by the positive chlorine ion as follows:[1]

$$\left.\begin{array}{l} 2\overset{-}{HO} \longrightarrow 2\overset{+}{H} + 2\overset{--}{O} \\ 2\overset{+}{Cl} \longrightarrow 2\overset{-}{Cl} + 4\,\oplus \end{array}\right\} \longrightarrow \overset{--}{O} + \overset{++}{O} = O_2$$

or summarized more briefly, $2\overset{-}{HO} + 2\overset{+}{Cl} \longrightarrow 2\overset{+}{H} + 2\overset{-}{Cl} + O_2$. It is evident that this oxidation could take place only in the presence of a very low concentration of hydrogen ions since concentrated solutions of hydrochloric acid on electrolysis yield no oxygen. A high hydrogen ion concentration obliterates the hydroxyl ion concentration. Consequently the positive chlorine ions combine with the negative chlorine ions to form molecular chlorine in concentrated solutions: $\overset{+}{Cl} + \overset{-}{Cl} \longrightarrow Cl_2$. Thus, the existence of positive chlorine ions at the anode accounts for the fact that dilute solutions of hydrochloric acid yield oxygen while concentrated solutions yield chlorine. Accordingly, if positive chlorine ions result from anodic oxidation of negative chlorine ions, then negative hydrogen ions may arise by cathodic reduction of positive hydrogen ions and, therefore, precede the liberation of molecular hydrogen according to the equation: $\overset{-}{H} + \overset{+}{H} \longrightarrow H_2$.

Analogously, negative hydrogen ions may be formed and function in the production of molecular hydrogen when metals interact with water or acids according to the general equation: M (a divalent metal) + $2\overset{+}{H} \longrightarrow \overset{++}{M} + H_2$, which is represented from the electronic standpoint as follows:

$$M = \overset{++}{M} + 2\,\ominus; \quad \overset{+}{H} + \ominus \longrightarrow H; \quad H + \ominus \longrightarrow \overset{-}{H}; \overset{+}{H} + \overset{-}{H} \longrightarrow H_2.$$

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[1] Nernst ("Theoretical Chemistry," English trans., 1911, p. 767) regards the action of chlorine upon oxygen ions, molecular oxygen being liberated, as analogous to action of chlorine on bromine ions. Electronic equation for latter: $(Cl_2 = \overset{+}{Cl}\,\overset{-}{Cl}) + 2\overset{-}{Br} \longrightarrow 2\,\overset{-}{Cl} + (\overset{+}{Br}.\overset{-}{Br} = Br_2)$.

In this connection, direct evidence of the existence of negative hydrogen is afforded by the hydrides of the metals, for example, sodium hydride, NaH. Reference should be made to the interaction of sodium, on the one hand, and of sodium hydride on the other, with water according to the equations (1) and (2), respectively:

$$(1)\quad 2\mathrm{Na} + 2\mathrm{HOH} \longrightarrow 2\mathrm{NaOH} + \mathrm{H_2}$$

$$(2)\quad \mathrm{NaH} + \mathrm{HOH} \longrightarrow \mathrm{NaOH} + \mathrm{H_2}$$

From an ionic standpoint these reactions are represented as follows:

$$(1)\quad 2\mathrm{Na} + 2\overset{+}{\mathrm{H}} \longrightarrow 2\overset{+}{\mathrm{Na}} + \mathrm{H_2}$$

$$(2)\quad \mathrm{NaH} + \overset{+}{\mathrm{H}} \longrightarrow \overset{+}{\mathrm{Na}} + \mathrm{H_2}$$

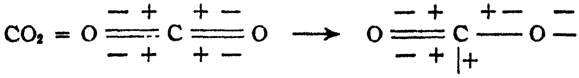
A further analysis of these reactions from an electronic standpoint requires that sodium be regarded as a compound of positive sodium with a negative electron, (Na $\ominus$), the interaction of which with water (or positive hydrogen ions) yields molecular hydrogen according to the general electronic scheme indicated above. Analogously sodium hydride is a compound of positive sodium with negative hydrogen, $(\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{H}})$, and the ionic equation (2) above is represented electronically as follows:

$$\mathrm{NaH} = \overset{+}{\mathrm{Na}}\text{——}\overset{-}{\mathrm{H}} \longrightarrow \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{H}};\quad \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{H}} \longrightarrow \mathrm{H_2}.$$

In other words, sodium hydride may be regarded as an ionogen which, dissociating yields positive sodium and negative hydrogen.[1]

Further evidence that the hydrogen of sodium hydride functions negatively is shown by the formation of sodium formate according to the equation: $\mathrm{NaH} + \mathrm{CO_2} \longrightarrow \mathrm{HCO_2Na}$.[2] It has been shown previously that each of the four valences of the carbon atom in carbon dioxide is positive while in formic acid one of the carbon valences is negative. It follows, therefore, that when sodium hydride combines with carbon dioxide one of the positive valences of the carbon atom in carbon dioxide is reduced to a negative valence by the negative hydrogen of sodium hydride. The negative hydrogen naturally tends to become positive and accordingly yields two electrons which are just sufficient to reduce one positive valence of carbon to a negative valence which, in turn, binds the resultant positive hydrogen atom:

$$\mathrm{NaH} \longrightarrow \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{H}};\quad \overset{-}{\mathrm{H}} \longrightarrow \overset{+}{\mathrm{H}} + 2\,\ominus$$



$$\mathrm{CO_2} = \mathrm{O}\overset{-\ +}{\underset{-\ +}{=\!=}}\mathrm{C}\overset{+\ -}{\underset{+\ -}{=\!=}}\mathrm{O} \longrightarrow \mathrm{O}\overset{-\ +}{\underset{-\ +}{=\!=}}\underset{|+}{\mathrm{C}}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-}{\text{—}}$$

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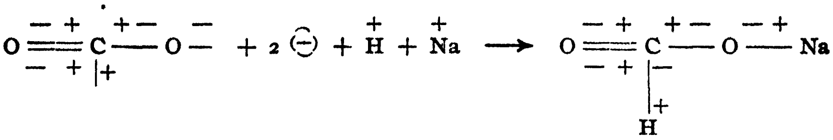
[1] Results of experiments on the electrolysis of hydrides of metals will be presented in a subsequent paper.

[2] Moissan, *Compt. rend.*, 136, 723 (1903).

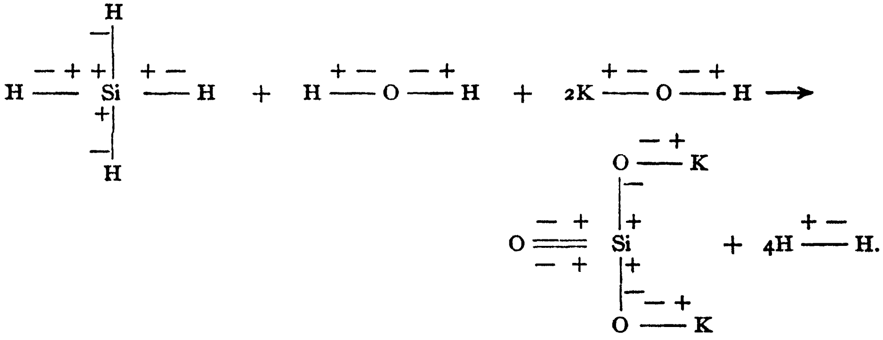


$$O\overset{-\ +}{\underset{-\ +}{=\!=}}\underset{|+}{C}\overset{+\ -}{-}O\overset{-}{-} + 2\ominus + \overset{+}{H} + \overset{+}{Na} \longrightarrow O\overset{-\ +}{\underset{-\ +}{=\!=}}\underset{\underset{H}{|-\,+}}{C}\overset{+\ -}{-}O\overset{-\ +}{-}Na$$

Again, the existence of negatively functioning hydrogen is shown by the interaction of silicon hydride and aqueous potassium hydroxide. One volume of the former yields four volumes of hydrogen according to the equation:

$$SiH_4 + HOH + 2KOH \longrightarrow K_2SiO_3 + 4H_2.$$

Now, potassium silicate is analogous in composition to potassium carbonate a derivative of carbonic acid in which each of the valences of the carbon atom functions positively. Therefore each of the valences of the silicon atom in potassium silicate functions positively. Furthermore since neither water nor potassium hydroxide acts as a reducing agent in the above equation, one must conclude that each of the four valences of silicon hydride is also positive. Therefore, the hydrogen atoms function negatively and the above reaction from an electronic standpoint may be represented as follows:



$$H\overset{-\ +}{-}\underset{\underset{H}{+|-}}{\overset{\overset{H}{-|+}}{Si}}\overset{+\ -}{-}H + H\overset{+\ -}{-}O\overset{-\ +}{-}H + 2K\overset{+\ -}{-}O\overset{-\ +}{-}H \longrightarrow O\overset{-\ +}{\underset{-\ +}{=\!=}}\underset{\underset{O\overset{-\ +}{-}K}{|+\,-}}{\overset{\overset{O\overset{-\ +}{-}K}{-|+}}{Si}} + 4H\overset{+\ -}{-}H.$$

In this connection it is worthy of note that silicon and carbon, from the standpoint of the periodic classification, belong to the same natural family. Therefore, since silicon may be united to negative hydrogen as shown above, it is natural to conclude that carbon also may hold in combination negatively functioning hydrogen. In other words, an interpretation of the evidence presented leads to the conclusion that hydrogen may function not only positively but also negatively. The possibility of negative hydrogen being held in combination by positive valences of the carbon atom is also warranted by the electronic formula for benzene, which renders possible interpretations of many apparently anomalous phenomena presented in previous papers. In this connection it should be recalled that in the rearrangement reactions which characterize the substituted nitrogen halides[1] the positive halogen atom, on passing from the nitrogen atom to the nucleus, invariably assumes a position para or ortho to the negative amino radical, and when the para and both ortho positions are occupied as in 2,4,6-trichloroacyl nitrogen halide, rearrangement is both experimentally and theoretically impossible. This constitutes a proof of the identity of polarity of the positions 2, 4, and 6 of the benzene nucleus, each of which is occupied by a positive halogen atom. Accordingly, the hydrogen atoms in positions 2, 4 and 6 must be assumed to function positively.

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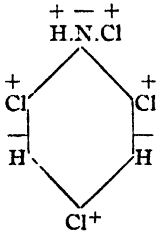
[1] Fry, THIS JOURNAL, 34, 667–8 (1912).



Now negatively functioning hydrogen has just been shown to act as a reducing agent, but *benzene in this sense is neither an oxidizing nor a reducing agent. Therefore, the number of positive hydrogen atoms of the nucleus must be equal to the number of negative hydrogen atoms of the nucleus.* In other words, if positions 2, 4 and 6 are occupied by positive hydrogen atoms, then positions 1, 3 and 5 must be occupied by negative hydrogen atoms. This conclusion may be regarded as a further substantiation of the proposed electronic formula for benzene.

The possibility of formulating a new definition for the so-called "nascent state" may now be considered. "Nascent action" according to common usage is a term[1] for "all those phenomena in which a substance at the moment of its liberation from compounds performs reactions it is incapable of in its ordinary condition. Thus, to cite a simple and well-known case: Hydrogen has no action on silver chloride suspended in a liquid through which it is bubbled; hydrogen evolved within the liquid (electrolytically or by action of metals) produces metallic silver, hydrochloric acid being formed at the same time." Such action has been attributed to the liberation of hydrogen in the atomic state. Accordingly, changes are effected by the atoms before they have coalesced to form molecules.

A more comprehensive view of the nascent state and nascent action may be developed by applications of the electronic conceptions of oxidation and reduction.

Ordinarily, hydrogen functions positively, while chlorine functions negatively ($HCl \rightleftarrows \overset{+}{H} + \overset{-}{Cl}$), but in certain compounds, or under special conditions, hydrogen may function negatively and chlorine positively. Furthermore, negative hydrogen has been shown to act as a reducing agent, since it naturally tends to revert to its ordinary state, positive hydrogen, which change is accompanied by the liberation of electrons. On the other hand, positive chlorine acts as an oxidizing agent, since it naturally tends to become negative by acquisition of electrons. In terms of the atomistic conception of electricity the latter change is equivalent to the liberation of the so-called "positive electrons." The following equations (1) and (2) illustrate, respectively, these natural tendencies:

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[1] Freund, "Study of Chemical Composition," Cambridge Physical Series, 1904, p. 327.

$$(1)\quad \overset{-}{\mathrm{H}} \longrightarrow \overset{+}{\mathrm{H}} + 2\ominus, \qquad (2)\quad \overset{+}{\mathrm{Cl}} \longrightarrow \overset{-}{\mathrm{Cl}} + 2\oplus.$$

An electrically neutral state, *i. e.*, the atomic state, may be encountered intermediately in each of the above changes and is indicated in the following equations (3) and (4), respectively:

$$(3)\quad \overset{-}{\mathrm{H}} \longrightarrow \mathrm{H} + \ominus, \qquad \mathrm{H} \longrightarrow \overset{+}{\mathrm{H}} + \ominus.$$

$$(4)\quad \overset{+}{\mathrm{Cl}} \longrightarrow \mathrm{Cl} + \oplus; \qquad \mathrm{Cl} \longrightarrow \overset{-}{\mathrm{Cl}} + \oplus.$$

Now, if the atomic state and nascent state are to be regarded as synonomous then they may be defined, from the electronic standpoint, as an unstable condition which manifests not only an adaptability but also a tendency to either gain or lose electrons and thereby attain a more stable condition. *This condition can not be limited to the atomic state of an element,* since not only atomic or neutral hydrogen, but also negative hydrogen tends to lose electrons. A comparison of equations (1) and (3) indicates that a negative hydrogen atom may be more potent as a reducing factor than a neutral hydrogen atom since the former yields two electrons while the latter yields only one in the transition to the positive state. The activity of negative hydrogen as a reducing agent has been illustrated by the action of sodium hydride upon carbon dioxide. It is the negative hydrogen, that is to say, nascent hydrogen, which in this case reduces carbonic acid to formic acid.

On the other hand, positive chlorine is a more active oxidizing agent than is atomic or neutral chlorine since the former unit may combine with two electrons while the latter unites with only one electron in the transition to negative chlorine, as indicated in equations (2) and (4) above. It has been shown that the formation of positive chlorine ions at the anode[1] would account for the liberation of oxygen during the electrolysis of very dilute hydrochloric acid (low hydrogen ion concentration) according to the abbreviated equation: $2\overset{+}{\mathrm{Cl}} + 2\overset{-}{\mathrm{OH}} \longrightarrow 2\overset{+}{\mathrm{H}} + 2\overset{-}{\mathrm{Cl}} + \mathrm{O}_2$. The same reaction may be involved in the oxidizing reactions of hypochlorous acid.

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[1] From this standpoint either negative or neutral hydrogen atoms produced at the cathode may be the active reducing agent in the so-called electrolytic reductions.

Therefore, from these points of view, the "nascent state" may be defined more comprehensively as *an unstable condition of a substance which manifests an adaptability and a tendency to lose electrons or to gain electrons and thereby revert to a more stable condition. If the substance (ion, atom, or compound) lose negative electrons it acts as a reducing agent. If it combines with negative electrons it acts as an oxidizing agent.* As a matter of fact practically all actions classed as "nascent" are of an oxidation or a reduction type.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE MOLECULAR REARRANGEMENT OF TRIARYLMETHYLHYDROXYLAMINES AND THE "BECKMANN" REARRANGEMENT OF KETOXIMES.[1]

BY JULIUS STIEGLITZ AND PAUL NICHOLAS LEECH.[2]

Received December 23, 1913.

Acid halogen amides[3] RCONH(Hal), hydroxamic acids RCONHOH, dihydroxamic acids[4] RCO.NH.OCOR, and acid azides[5] $RCON_3$ undergo readily, under the influence of appropriate reagents, molecular rearrangements as the result of which derivatives of the amines RNH_2 are formed. According to the theory of one of us[6] all of these rearrangements may be interpreted as resulting from the primary formation and subsequent rearrangement of a *univalent* nitrogen derivative, acyl imide, RCO.N<. The reagents used for effecting the rearrangement are in each instance those one would expect to use on the basis of this theory to facilitate the formation of the univalent nitrogen derivative and bring about the rearrangement. Thus, in Hofmann's rearrangement of acid halogen amides, bases are used and the reaction is interpreted as following the course:[1]

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[1] See a preliminary report (abstract) by Stieglitz, Reddick and Leech, *VIII Internat. Congr. Appl. Chem.*, 25, 443 (1912), and by Stieglitz and Leech, *Ber.*, 46, 2147 (1913).

[2] The work presented in this paper forms the basis of a dissertation by Leech presented to the University of Chicago in part fulfilment of the requirements for the Ph.D. degree.

[3] A. W. Hofmann, *Ber.*, 14, 2725 (1882); 15, 408 (1883); Hoogewerff and van Dorp, *Rec. trav. chim.*, 6, 373 (1887); 8, 173 (1889), etc.; Lengfeld and Stieglitz, *Am. Chem. J.*, 15, 215, 504 (1893), etc.

[4] Lossen, *Ann.*, 161, 359 (1872), etc.; Thiele and Pickard, *Ibid.*, 309, 189 (1899); and especially L. W. Jones, *Am. Chem. J.*, 48, 1 (1912).

[5] Curtius, *Ber.*, 27, 778 (1895); *J. prakt. Chem.*, 50, 289 (1894), etc.

[6] Stieglitz, *Am. Chem. J.*, 18, 751 (1896); 29, 49 (1903); Stieglitz and Earle, *Ibid.*, 30, 399, 412 (1903); Stieglitz and Slossen, *Ber.*, 34, 1613 (1901); Slossen, *Am. Chem. J.*, 29, 289 (1903); Hilpert, *Ibid.*, 40, 155 (1908); Stieglitz and Peterson, *Ber.*, 43, 782 (1910); Peterson, *Am. Chem. J.*, 46, 325 (1911); Stieglitz and Leech, *loc. cit.*; Stieglitz and Vosburgh, *Ber.*, 46, 2151 (1913); Schroeter, *Ber.*, 42, 2340 (1909); 44, 1207 (1911); Stoermer, *Ibid.*, 42, 3133; Wieland, *Ibid.*, 42, 4207 (1909); Montague, *Ibid.*, 43, 2014 (1910); L. W. Jones, *Am. Chem. J.*, 48, 1 (1912).

$$\mathrm{RCONHBr + NaOH \longrightarrow RCONNaBr + HOH \longrightarrow}$$
$$\mathrm{RCO.N\!< + NaBr + HOH \longrightarrow CO:NR + NaBr + H_2O} \quad (1)$$

and

$$\mathrm{CO:NR + 2NaOH \longrightarrow RNH_2 + Na_2CO_3 + H_2O} \quad (2)$$

Isocyanates CO : NR have indeed been the first isolated[2] products of this rearrangement. For dihydroxamic acids, bases are also used to effect the rearrangement, the salts formed decomposing in a way analogous to that indicated for the halogen amides, and again, isocyanates have been observed as the first product of the rearrangement.[3] For hydroxamic acids, RCO.NHOH, dehydrating agents or dry distillation are employed, and with acid azides $\mathrm{RCO.N_3}$ gentle heat alone is sufficient to cause an evolution of nitrogen, leading to the formation of isocyanates[4] and their derivatives (*e. g.*, of urethanes when azides are warmed with alcohols). Where the formation of univalent nitrogen is interfered with, as in the case of alkyl derivatives RCO.NR'(Hal)[5] and RCO.NR'OH,[6] no corresponding rearrangement has heretofore been brought about by the reagents and under the conditions effective with the nonalkylated compounds.

When the above theory was developed it was recognized that certain important questions remained to be solved in connection with it.[7] A number of these have already been answered[8] by the investigations carried on continuously in this laboratory. One of the most important of the problems still under investigation[9] from several sides is that of the theory of the rearrangement of ketoximes, a rearrangement discovered and first investigated by Beckmann.[10] The work reported on in this paper is intended to throw some further light on this problem.

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[1] Stieglitz, *loc. cit*

[2] Hofmann, *Ber.*, **15**, 412 (1882). Dry salts of the acid halogen amides decompose, when warmed, forming isocyanates (unpublished work of Stieglitz and O. Eckstein, 1905).

[3] L. W. Jones, *loc. cit.*

[4] Schroeter, *Ber.*, **42**, 2336 (1911).

[5] Stieglitz and Slossen, *loc. cit.*

[6] Stieglitz and O. Higbee, *Am. Chem. J*, **29**, 52 (1903).

[7] *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903); see also L. W. Jones, *loc cit*, pp. 23, 28.

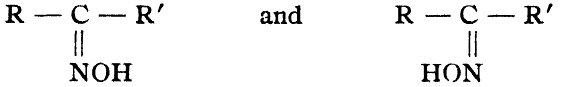
[8] Stereoisomeric chloroimido esters were prepared and investigated to determine the relation of stereoisomerism to the rearrangement of acid halogen amides (Stieglitz and Earle, Hilpert, *loc. cit.*) and stereoisomeric chloroimidoketones were prepared to investigate the same relations in connection with ketoximes (Stieglitz and Peterson, *loc. cit.*).

[9] Stieglitz and Peterson, *loc. cit.*; Stieglitz and Watkins, Reddick, Leech, Vosburgh, Senior (unpublished work).

[10] *Ber.*, **19**, 988 (1886); **20**, 1507, 2508 (1887), etc.

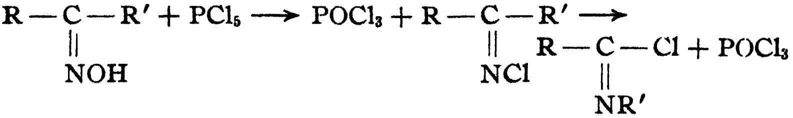
The Rearrangement of Ketoximes.

Ketoximes suffer the "Beckmann" rearrangement when they are treated with any one of a variety of reagents, such as phosphorus pentachloride, concentrated sulfuric acid, acetic anhydride, etc. These reagents have in common the property that they are dehydrating agents. A further, very important fact observed is that *stereoisomeric* oximes



$$\text{R}-\underset{\underset{\text{NOH}}{\|}}{\text{C}}-\text{R}' \quad \text{and} \quad \text{R}-\underset{\underset{\text{HON}}{\|}}{\text{C}}-\text{R}'$$

give, according to Beckmann,[1] primarily derivatives of such amines as would result from a *direct exchange* of the OH group and the radical R or R'. *immediately opposite* to the OH group in the configuration of the stereoisomer. Beckmann assumed,[2] as regards the mechanism of this interesting reaction, that such a direct exchange takes place, without the formation of any intermediate products. He compared the exchange with the well-known exchange of *ions* between molecules, the atoms being considered as held in the molecules by electrical forces.[3] Actual ionization of ketoximes, in the direction indicated, has never been detected and Beckmann did not postulate any measurable ionization. Beckmann's theory is further characterized by ascribing the rearrangement to a "catalytic" action of the rearranging agents. But, according to modern theory, catalyzers act in a specific and definite way upon the catalyzed substances, either physically (*e. g.*, as solvents, with attendant changes in condition, dissociation, etc.) or chemically, forming "intermediate products." The very intimate relation between the *chemical* nature of the rearranging compounds and of the reagents used, as indicated above, shows clearly that the action of the reagents is essentially *chemical* and that we must look for intermediate products, resulting from the action of the reagents, for the explanation of the rearrangement. A number of chemists have in fact assumed that intermediate products are first formed, which then undergo the actual molecular rearrangements. Thus, Hantzsch[4] assumes that the ketoximes form with phosphorus pentachloride chloroimides, which then rearrange by a direct exchange of chlorine and the radicals R or R':



$$\text{R}-\underset{\underset{\text{NOH}}{\|}}{\text{C}}-\text{R}' + \text{PCl}_5 \longrightarrow \text{POCl}_3 + \text{R}-\underset{\underset{\text{NCl}}{\|}}{\text{C}}-\text{R}' \longrightarrow \text{R}-\underset{\underset{\text{NR}'}{\|}}{\text{C}}-\text{Cl} + \text{POCl}_3 \qquad (3)$$

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[1] *Ann.*, **252**, 44 (1889); **274**, 1 (1892); **296**, 279 (1897), etc.

[2] *Ber.*, **27**, 300 (1894). He originally (*Ber.*, **19**, 988 (1886)) made the same assumption as Hantzsch did later (see further on in the text).

[3] No discussion of the specific charges on the various atoms was entered into. Later on in this paper an attempt is made to shed light on this all-important detail on the basis of the experimental results obtained by us.

[4] *Ber.*, **24**, 3516 (1891).

To test this view Stieglitz and Peterson[1] prepared from imidoketones and hypochlorous acid, chloroimido ketones of the structure indicated. They succeeded also in obtaining stereoisomeric chloroimidoketones, corresponding to the stereoisomeric oximes. But these were found, in every instance, to be stable and not to rearrange up to temperatures of 100° to 120°, the highest temperatures used, because the "Beckmann" rearrangements occur far below these temperatures. In fact, every effort to rearrange these chloroimido ketones under any conditions has, thus far, been futile.[2] The conclusion was drawn that chloroimido ketones could not be the intermediate products undergoing the "Beckmann" rearrangement.

It is necessary now to discuss another possibility in this connection, that has recently suggested itself as the result of the important work of W. A. Noyes[3] on the possible existence of *electromeric* nitrogen chlorides NCl_3. It is possible that the chloroimides obtained by Stieglitz and Peterson are *electromers* of the chloroimides supposed to be intermediate products in the rearrangement of ketoximes by phosphorus pentachloride. The chloroimido ketones prepared by us, according to their method of preparation and especially according to their behavior, were recognized by us[4] as derivatives of *positive chlorine*[5] $RR'C^{++} : N^{---}Cl^{+}$.[6] They are prepared from imido ketones by the action of hypochlorous acid

$$RR'C^{++} : {}^{--}N^{-} - {}^{+}H + HO^{-} - {}^{+}Cl \longrightarrow RR'C^{++} : {}^{--}N^{-} - Cl^{+} + H_2O. \quad (4)$$

They yield again, by hydrolysis, hypochlorous acid (a proof that the chlorine has not changed its charge[7]) and they are strong oxidizing agents (*e. g.*, $RR'C : N^{-}Cl^{+} + 2{}^{+}HI^{-} \longrightarrow RR'C : N^{-}H^{+} + I^{+}.I^{-} + {}^{+}HCl^{-}$, a second proof that the chlorine has not changed its charge). Now, oximes are not infrequently obtained by the action of *nitrous acid* on organic compounds: such is the case, for instance, for oximido mesoxalic esters and quinone oxime, which may be obtained from malonic esters and phenol, respectively, by the action of nitrous acid, as well as from the ketones by the action of hydroxylamine. Oximes[1] could, consequently have besides the probable electronic structure $RR'C^{++}:{}^{--}N^{-}-{}^{+}O^{-}-{}^{+}H$ also the structure of a nitrous acid derivative $RR'C^{--}:{}^{++}N^{+-}O^{-+}H$. A compound of the latter structure could form with phosphorus pentachloride a chloride corresponding to nitrosyl chloride $O^{--}={}^{++}N^{+}-{}^{-}Cl$. The products $RR'C^{--}:{}^{++}N^{+}-Cl^{-}$ would be *electromers* of the chloroimido ketones, prepared by Stieglitz and Peterson, and could *possibly* suffer a rearrangement into $RC^{+++}({}^{-}Cl):{}^{--}N^{-}R'^{+}$ or $R'C^{+++}({}^{-}Cl):{}^{--}N^{-}R^{+}$, involving, it is true, a complex and *unlikely* shifting of charges! But such an assumption that these electromers of the non-rearranging chloroimides of Stieglitz and Peterson might undergo the "Beckmann" rearrangement of ketoximes is altogether in conflict with the facts and highly improbable, although it must be taken into account. As is shown by the rearrangement of acid halogen amides $R.CO.NH(Hal^{+})$, it is just the *positive* halogen derivatives which are known to rearrange readily, and most likely the ultimate reason for the disturbance of the valences (electrons), which results in the rearrangement, is the tremendous tendency of positive chlorine and positive bromine to capture electrons in order to form their stable negative ions Cl^{-} and Br^{-} (see below, page 280). Consequently, of the series of electromeric chloroimido ketones, the chloroimides of Stieglitz and Peterson *should be the rearranging ones* and they do *not rearrange.*

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[1] *Loc. cit.*

[2] Stieglitz and Peterson, *loc. cit.*; unpublished work by Stieglitz and P. H. Watkins; Vosburgh, see a later article in THIS JOURNAL. These results do not exclude the possibility that in the future some means may be found to effect their rearrangement and new methods are being tried by us from time to time (cf. *Ber.*, **46**, 2151 (1913) and Vosburgh, *loc. cit.*).

[3] THIS JOURNAL, **35**, 767 (1913); see also Nelson and Falk, *Ibid.*, **32**, 1637 (1910); and **33**, 1140 (1911).

[4] *Ber.*, **43**, 782 (1910); cf. Seliwanow, *Ber.*, **25**, 3617 (1892); Lengfeld and Stieglitz, *loc. cit.*; L. W. Jones, *loc. cit.*

[5] Cf. W. A. Noyes, THIS JOURNAL, **23**, 460 (1901); Stieglitz, *Ibid.*, **23**, 796 (1910); Walden, *Z. physik. Chem.*, **43**, 385 (1903).

[6] Only the significant charges are indicated in all of the electronic structures used.

[7] Seliwanow, Lengfeld and Stieglitz, L. W. Jones, *loc. cit.*; Stieglitz, THIS JOURNAL, **23**, 796 (1901). Since this was written, Nelson, Beans and Falk (THIS JOURNAL, **35**, 1810 (1913)) have emphasized the value of this method of determining the nature of the charge on an atom.

Hence this possibility of electromeric chloroimido ketones, of the nature indicated, does not help out the theory of Hantzsch regarding the "Beckmann" rearrangement. In fact, a direct exchange of chlorine and a radical R or R′ under these circumstances not only offers no advantages over the assumption made by Beckmann of a direct exchange of OH against the radicals, but has the very great disadvantage, as we have just seen, of being obliged to assume a far more thorough-going and complicated shifting of electrons than is necessary in the Beckmann theory. This can only be avoided by assigning to the intermediate product, the chloroimide, an electron structure which belongs to the product obtained by Stieglitz and Peterson, and, as stated, this does not suffer rearrangement.

Further on it will be shown how our present work has led us to consider a *third* electromer of the chloroimido ketone, the assumption of the formation of which as an intermediate product in the rearrangement of ketoximes by phosphorus pentachloride might solve all the problems involved in this reaction.

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[1] Cf. Nelson and Falk, *loc. cit.*

In the application of Stieglitz's theory of the formation of a rearranging univalent nitrogen derivative as an intermediate product to the rearrangement of ketoximes under the influence of phosphorus pentachloride, it was assumed[1] that there is a preliminary addition of hydrogen chloride (always present in the ethereal solutions used) to the oximes and that a subsequent loss of water leads to the formation of the rearranging univalent nitrogen derivative. For benzophenone oxime we have:

$$R_2C:NOH \xrightarrow{+HCl} R_2CCl(NHOH) \xrightarrow{-HOH} R_2CCl.N: \longrightarrow RCCl(:NR) \quad (5)$$

Benzochloroanilide is the first isolated product of the action. The addition of hydrogen chloride to the double bond between the carbon and nitrogen would tend to destroy *stereoisomeric differences* due to the double bond, and therefore a more extended and closer investigation of the relation between stereoisomerism and rearrangement, as observed by Beckmann (see above), was pointed out as being necessary before the theory of univalent nitrogen could be finally accepted as applying to the rearrangement of ketoximes.[2] The stereoisomeric chloroimido ketones, prepared by us as a first step to investigate these relations, would not rearrange at all, as has been explained above, and did not throw the light expected on this phase of the problem. In the meantime important work by Schroeter,[3] on the rearrangement of stereoisomeric ketoximes, showed that different products are obtained from stereoisomers according to the nature of the reagents used and the conditions of the experiment, confirming the suspicion originally entertained[2] that closer investigation might remove the apparent contradiction between the behavior of stereoisomers and our theory. Schroeter indeed considers that all of his experimental work agrees with this theory.

In spite of this and further important work by other investigators confirming the theory (besides Schroeter, Wieland,[1] Stoermer,[1] and L. W. Jones[1] have recently found valuable confirmatory evidence), we have considered it necessary to continue our investigations into the nature of these typical rearrangements, particularly as a way has shown itself which promises to reduce these problems to their simplest possible terms, by the systematic investigation of rearrangements of triphenylmethylhydroxylamine and related compounds.[4] Our newest results have indeed brought to light facts which indicate the necessity of a broader theoretical basis (see below) than has hitherto been deemed necessary.

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[1] *Loc. cit.*

[2] See Stieglitz, *Am. Chem. J.*, 18, 754 (footnote) (1896). Montagne (*Ber.*, 43, 2014 (1910)) has criticized the theory because of the same facts outlined in the text. From the outset, as the above footnote shows (cf. L. W. Jones, *Am. Chem J*, 48, 28 (1912)) this complication was recognized, only it was considered that the relation of stereoisomerism to the rearrangement was not so firmly established that it should be allowed to discourage a more critical investigation of these relations on the basis of the univalent nitrogen theory of rearrangement.

[3] *Ber.*, 43, 2014 (1910); see also Schroeter, 42, 2336 (1909); 44, 1207 (1911).

[4] Parallel with the work reported by us are investigations by Miss Isabelle Vosburgh on triphenylmethylhalogenamines $(C_6H_5)_3CNH(Hal)$ and $(C_6H_5)_3CN(Hal)_2$ and re-

The Rearrangement of Triphenylmethylhydroxylamine.

Triphenylmethylhydroxylamine $(C_6H_5)_3C.NHOH$ has the same kind of structure as was assumed for the hydrogen chloride addition product $(C_6H_5)_2CCl(NHOH)$ in the rearrangement of benzophenone oxime (see equation 5, above)—its examination therefore eliminated the need of any assumption on one phase of the problem. Furthermore, it and its analogs are in every way the simplest products yet investigated in regard to these rearrangements—they are saturated in regard to the carbon valences (oximes and chloroimides are not) and they do not contain, outside of the hydroxylamine or analogous group,[1] any reactive group (acid halogen amides and similar compounds have reactive C : O groups) or reactive hydrogen (as in tautomeric forms[2] of acid chloroamides, etc.). Finally, the nature of the charges on the various radicals can be more convincingly determined than in the case of acid derivatives.

Four problems of special interest have been included in the scope of the present investigation of these compounds and their derivatives. The first problem consisted in determining whether any rearrangement at all could be effected and what reagents would be effective. The second problem was the investigation of possible rearrangements of derivatives like $(C_6H_5)_3C.N(CH_3)OH$ which could not readily form any univalent nitrogen derivative. In the third place, the behavior of benzoyltriphenylmethylhydroxylamine was studied, one of the hydrogen atoms of the hydroxylamine group being replaced by the benzoyl radical, in place of by a methyl group as in the case just discussed. Finally, as a fourth problem, the relation of the positive and negative character of radicals (C_6H_4X), etc., in the rearrangement of compounds $(C_6H_4X)(C_6H_4Y)(C_6H_4Z)C.NHOH$, etc., to the question as to *which* radical or radicals *migrate* from the carbon to the nitrogen in a rearrangement was investigated as a necessary basis for distinguishing such influences from stereoisomeric effects in the study of the rearrangement of stereoisomeric oximes $(C_6H_4X)(C_6H_4Y)C : NOH$.

In regard to the first problem, we have found[3] that triphenylmethyl-

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lated compounds, and by Mr. James K. Senior on triphenylmethylhydrazines and hydrazones of ketones, etc. It is interesting that closely related as are hydrazine and hydroxylamine derivatives, no rearrangement, of this type, of the hydrazines seems as yet to have been accomplished, whereas, hydroxylamines rearrange easily (the benzidine rearrangements, etc., are of a different type).

[1] NH(Hal), etc.

[2] See Stieglitz and Vosburgh, *loc. cit.*

[3] The first observation was made by Stieglitz and Guy Reddick in 1909–1910. Mr. Reddick's illness compelled him to abandon his work and it was continued by Mr. Leech.

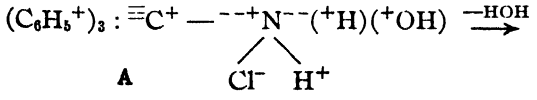
hydroxylamine and chlorotriphenylmethylhydroxylamine are in fact readily (practically quantitatively) rearranged by phosphorus pentachloride under exactly the same conditions that are used in the rearrangement of benzophenone oximes. We have, apparently,

$$(C_6H_5)_3C.NHOH \xrightarrow{-HOH} (C_6H_5)_3C.N \longrightarrow (C_6H_5)_2C : NC_6H_5. \quad (6)$$

The product, phenylimido benzophenone, was identified by a comparison with a synthetic preparation, by analysis and by the products of its hydrolysis, aniline and benzophenone. Occasionally[1] a slight *decomposition* of triphenylmethylhydroxylamine by phosphorus pentachloride, or by the hydrogen chloride formed in the main action was observed:

$$(C_6H_5)_3C.NHOH + HCl \longrightarrow (C_6H_5)_3CCl + NH_2OH \quad (7)^2$$

With other reagents employed to rearrange oximes, such as acetic anhydride and Beckmann's reagent, this kind of *decomposition* was found to become the chief action and no rearrangement products were observed. On the other hand, when solid triphenylmethylhydroxylamine *hydrochloride* was treated with phosphorus pentoxide, the rearrangement expressed in equation 6 was again easily accomplished. We believe this is the first time that this dehydrating agent *par excellence* has been used to effect this type of rearrangement. The result raises an interesting question, which must be considered here particularly because of its relations to the behavior of N-methyl-triphenylmethylhydroxylamine (see below) and to the problem of the influence of stereoisomerism on the rearrangement of *ketoximes*: does the phosphorus pentoxide act on the *free base* of decomposed triphenylmethylhydroxylamine hydrochloride, forming triphenylmethylimide $(C_6H_5)_3C.N$ as a rearranging intermediate product, or can it affect the hydrochloride itself as follows:[3]



$$(C_6H_5^+)_3 : {}^{\equiv}C^+ \text{---}{}^{+}\underset{Cl^- \quad H^+}{N}{}^{--}(^+H)(^+OH) \xrightarrow{-HOH}$$

A

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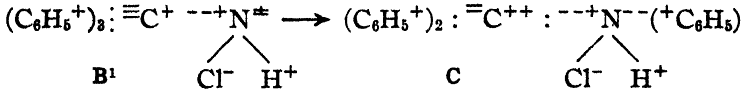
[1] Work with Reddick.

[2] The action was recognized by the formation of some triphenylcarbinol and its ethyl ether by the treatment of the reaction product with alcohol and water. Possibly a derivative such as $(C_6H_5)_3C.NHOPCl_4$ is first formed (see Werner, *Ber.*, 25, 40 (1892)).

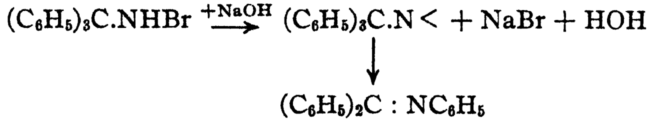
[3] Only the significant charges are indicated. Triphenylmethyl chloride and its derivatives are considered to have *positive phenyl* groups attached to the methyl carbon atom, as is indicated in equation 8. One of the most convincing pieces of evidence in favor of this assumption is the following: if triphenyl carbinol had the electronic structure $(C_6H_5^-)_3{}^{+++}C^{+-}O^-H^+$, it would be a *pronounced acid*, the positive charges on the methyl carbon atom repelling the positive hydrogen and causing it to ionize (cf. W. A. Noyes, THIS JOURNAL, 34, 663 (1912)). Triphenyl carbinol is no pronounced acid, but shows a tendency to exchange its OH group rather easily for other negative radicals (Cl^-, etc.)—which is to be expected from $(C_6H_5^+)_3{}^{\equiv}C^{+-}O^-H^+$.



$$(C_6H_5^+)_3{:}{}^{\equiv}C^+\;{}^{--+}\underset{Cl^-\;\;H^+}{N^{\pm}} \longrightarrow (C_6H_5^+)_2 : {}^{=}C^{++} : {}^{--+}\underset{Cl^-\;\;H^+}{N^{--}}(^+C_6H_5) \quad (8)?$$

B[1] C

We note that the OH group in the compound **A** is considered to be positive, as it most probably is in hydroxylamine, and surely is for one of the two hydroxyl groups in hydrogen peroxide,[2] and as chlorine and bromine are in the corresponding triphenylmethylhalogen amines and in all their other halogen amine derivatives. In the formation of water, containing the stable *negative* hydroxyl, the oxime hydroxyl deprives the nitrogen atom of two electrons,[3] leaving the product **B.** The rearrangement of **B** takes place as follows: first the migration of two electrons from the carbon atom to the nitrogenatom gives the latter a normal, stable charge, such as it has in ammonium salts: the resulting positive charge on the carbon can not hold one of the positive phenyl groups, which, following the electrical field of force from the negatively charged nitrogen, moves to the latter, thus consummating the rearrangement:[4] the remaining negative charge on the nitrogen holds the new positive charge on the carbon atom, a double bond resulting. In other words, the compound **B** would be a *hydrochloride* of *triphenylmethylimide* $(C_6H_5)_3C.N^{\pm}$ or $(C_6H_5)_3C.N$ and if it *could exist* even for a very short time,[5] it *might well have the latter's property of causing a rearrangement in the manner indicated.* The compound **B** would also be an *electromer* of triphenylmethylchloroamine $(C_6H_5)_3C.NH(Cl^+)$. This substance itself has not been prepared,[6] but the corresponding bromoamine $(C_6H_5)_3C.NH(Br^+)$ has been prepared by Miss Vosburgh and one of us.[7] By the action of soda lime it is rearranged:



$$\begin{array}{l}(C_6H_5)_3C.NHBr \xrightarrow{+NaOH} (C_6H_5)_3C.N< + NaBr + HOH \quad (9)\\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad (C_6H_5)_2C : NC_6H_5\end{array}$$

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[1] We may also assign to B the structure $(C_6H_5^+)_3{\equiv}C^{+-}\underset{\wedge}{N}^{-+}(H^+Cl^-)$.

[2] Many analogies between hydrogen peroxide, hydroxylamine and hydrazine ($H_2N^- - {}^+NH_2$, Stieglitz and Curme, *Ber.*, **46,** 911 (1913)) agree with this assumption; cf. Angeli, *Chem. Zentr.*, **1910,** II, 861.

[3] Stieglitz, *loc. cit.*; L. W. Jones, *loc. cit.*

[4] Similar series of changes, applied to univalent nitrogen intermediate products, represent the "electronic" expression of the molecular rearrangements of halogen amides, azides, oximes, etc., from the point of view of the theory of the univalent nitrogen intermediate product.

[5] See Stieglitz and Curme, *loc. cit.* and THIS JOURNAL, **35,** 1143 (1913), for evidence of the temporary existence of nitrogen radicals of low nitrogen valence; see also Wieland, *loc. cit.*

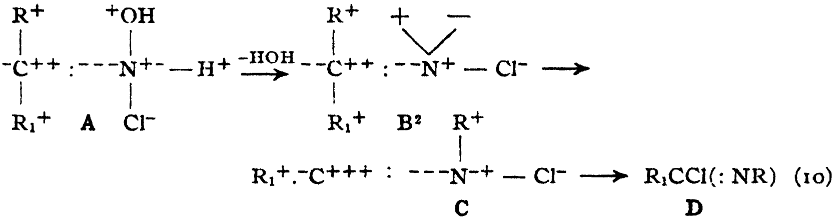
[6] The dichloroamine, $(C_6H_5)_3C.NCl_2$ is formed in attempts to prepare the chloroamine.

[7] *Ber.*, **46,** 2151 (1913).

but it does not rearrange without the loss of hydrogen bromide—in other words, it has different properties from the hypothetical substance **B**. The same difference would undoubtedly exist between **B** and the electromeric substance $(C_6H_5)_3C.NH(Cl^+)$. The problem of the possibility even of the momentary existence of such an electromeric substance as **B**, with different properties from those of the more stable chloroamine, is a problem of the future: the probability of such relations would be tremendously increased, if Noyes should confirm his preliminary indications of electromeric nitrogen trichlorides, but, even if final confirmation of such indications should not be forthcoming, considerations of this character are in themselves justified and must be dealt with, if progress is to be made in the study of the mysteries of structure and of rearrangements in organic chemistry.[1]

A New Interpretation of the Rearrangement of Ketoximes.

Should the momentary existence and the properties of the compound **B** in the rearrangement of triphenylmethylhydroxylamine hydrochloride by phosphorus pentoxide prove to be valid and reasonable assumptions, then the "Beckmann" rearrangement of benzophenone oxime and similar *oximes* might be formulated as follows in a perfectly analogous fashion:



$$\underset{R_1^+}{\overset{R^+}{{}^{-}{}^{-}C^{++}}} :{}^{-}{}^{-}{}^{-}\underset{\mathbf{A}\quad Cl^-}{\overset{{}^{+}OH}{N^{+-}}}-H^+ \xrightarrow{-HOH} \underset{R_1^+}{\overset{R^+}{{}^{-}{}^{-}C^{++}}} :{}^{-}{}^{-}\underset{\mathbf{B}^2}{\overset{+\ \vee\ -}{N^+}}-Cl^- \longrightarrow$$

$$R_1^+.{}^{-}C^{+++} : {}^{-}{}^{-}{}^{-}\underset{\mathbf{C}}{\overset{R^+}{N^{-+}}}-Cl^- \longrightarrow \underset{\mathbf{D}}{R_1CCl(:NR)} \quad (10)$$

We note that it is assumed, as usual, that the hydroxide group in the oxime is positive, that its great tendency to change into the exceedingly stable ordinary negative hydroxide group, as found in water, acids and bases, leads to the formation of water under the influence of dehydrating agents, the nitrogen atom losing thereby two electrons to the oxygen atom. The product **B** is an ammonium salt with two of the nitrogen valences unsaturated in the same way as they are unsaturated in univalent nitrogen derivatives and the salt **B** is obviously of the same type as the product **B** in equation 8. It is these unsaturated valences, again, which are considered to be the direct cause of the rearrangement, two electrons passing from the carbon atom to the nitrogen, to give this a normal and stable charge such as it has in ammonium salts. With the change of electronic forces, the positive radical R, *nearest*[1] *to the field of force,* is lost by the now positive carbon and carried to the now negative nitrogen. Such a series of actions would account for the nature and action of the reagents used to accomplish the rearrangement (acid dehydrating agents) and it gives a rational picture of the electrical forces in play in the rearrangement of the valences of the molecule. Such a course would *also* account for the *influence* of *stereoisomerism* on the rearrangement,[2] if such an influence should finally be established as beyond doubt—the radical (R in the above illustration) nearest to the electrical fields of force produced by the migration of electrons from carbon to nitrogen passing under the influence of this force to the nitrogen.

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[1] The electrolysis of salts of organic acids yields results fundamentally similar to those of the Hofmann-Lossen-Curtius-Beckmann rearrangements, a parallel which the one of us has had in mind for years and which seems of sufficient interest to present at this point because it connects the electronic explanation of the rearrangements with similar effects of an electric current, *i. e.*, of a current of electrons. As far as we know the relation has never, as yet, been pointed out, although Nef discusses the rearrangement and the electrolytic decompositions from the point of view of methylene reactions. Characteristic both for the rearrangements we are discussing and for the results of electrolysis, for instance of sodium acetate, is that carbon radicals are separated from a carbon atom which is directly linked to atoms of abnormal valence (univalent nitrogen, univalent oxygen; bivalent nitrogen may possibly have the same effect (see below)). We have $RCO.N : \longrightarrow CO : NR$ and $H_3C.CO.O^- + \oplus \longrightarrow H_3C.CO.O-$, and $2H_3C.CO.O- \longrightarrow 2CO : O + H_3C.CH_3$ or $2H_3C.CO.O- \longrightarrow H_3C.CO.OCH_3 + CO : O$. The interpretation of these equations from the electronic point of view as involving essentially migrations of electrons from carbon atoms to the univalent oxygen is obvious.

[2] The nitrogen may also be considered to be $: {}^{-}{}^{-}\overset{\vee}{N}{}^{+}Cl^-$.

The interpretation, as is evident, is an extension of the original theory of the one of us, assuming, as it does, the rearranging power of an intermediate hydrochloride of a univalent nitrogen derivative, acting in place of the ordinary free univalent nitrogen compound. The new view would by no means exclude the old, which has had such wide confirmation in the behavior of chloroamides, azides, hydroxamic acids, etc. *In the case of the ketoximes* the older view of an addition of hydrogen chloride to the double bond between the carbon and nitrogen (see p. 277) would account, as a *parallel action,* for results such as Schroeter obtained,[3] where *stereoisomeric influences were largely destroyed.* Further, the rearranging product **B** would be a third electromer of the chloroimido ketones of Stieglitz and Peterson (see p. 276), and would represent a logically active form of the chloride which Hantzsch assumed as the intermediate product in the rearrangement of ketoximes. This fundamental difference between the latter's theory and the one now developed should be carefully noted: Hantzsch assumes a direct exchange of R and Cl in the rearrangement, the new view assigns the rearranging power to *free valences* of the nitrogen atom, comparable with the free valences of univalent nitrogen.

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[1] The stereochemical nature of the isomerism of oximes is assumed.

[2] Schroeter, *Ber.*, **44**, 1208 (1911) has made suggestions along another line to account for such an influence.

[3] *Loc. cit.*

The. Rearrangement of N-Methyltriphenylmethylhydroxylamine.

The considerations just outlined become of prime importance in connection with the results of our work on the second problem investigated in this research, the problem of the rearrangement of N-methyltriphenylmethylhydroxylamine, $(C_6H_5)_3C.N(CH_3)OH$. When the non-methylated derivative is acted upon by phosphorus pentachloride in ether solution, the compound is rearranged in twenty to thirty minutes and practically quantitatively at the temperature of boiling ether. Under the same conditions and acted upon for the same time, its methyl derivative is hardly affected, most of it being recovered as the hydrochloride. If the action is continued for two or three hours, most of the substance (over 75%) is decomposed into triphenylmethylchloride[1] and methylhydroxylamine (see equation 7):

$$(C_6H_5)_3C.N(CH_3)OH + 2HCl \longrightarrow (C_6H_5)_3CCl + H_2N(CH_3)OH.Cl \quad (11)$$

But in the reaction products the presence of a small amount of a derivative of *methylaniline* could also be recognized. By hydrolysis of the reaction product by hydrochloric acid, a solution was obtained in which methylaniline was identified, not only by its characteristic reaction with hypochlorite, described in a recent paper,[2] and by its reaction with nitrous acid, but also by the preparation of acetomethylanilide. From a gram of substance, only enough acetomethylanilide was obtained for a few melting-point determinations of the recrystallized substance, but the identification was supported by the fact that the melting point of the product was not depressed when some of the substance was mixed with an equal amount of pure synthetic acetomethylanilide. Saponification of the substance thus identified gave a solution still showing the hypochlorite test for methylaniline. Other trials of the effect of phosphorus pentachloride on methyltriphenylmethylhydroxylamine led to the same result—in every case the main action was that of decomposition and only enough methylaniline was formed to be identified by the above tests, not enough to be isolated. With other agents of rearrangement, decomposition without the formation of any methylaniline resulted.

A supply of methylhydroxylamine, necessary for the preparation of N-methyl-triphenylmethylhydroxylamine on a large scale, has been ordered and the investigation of the action of phosphorus pentachloride on it will be continued, to verify the result obtained[3] and to find the conditions, if possible, for the formation of the methylaniline derivative as a main product, or in sufficient quantity for the isolation of methylaniline. From the work thus far done the following conclusions are worthy of special considerations: (1) The formation of a methylaniline derivative, as just described, seems to represent the first instance on record of the rearrangement of an alkylderivative N(alkyl)X of a hydroxylamine or halogen amine (X = OH, Cl or Br), corresponding to the rearrangement of the nonalkylated derivatives (—NHX). Although the formation of only very small quantities of a methylaniline derivative is indicated, this discovery—when verified by us[1]—must be taken into consideration in any theory of the Hofmann-Beckmann-Lossen-Curtius rearrangements that have been discussed in this paper. The observation clearly shows the necessity of further exhaustive investigations of analogous substances. (2) The contrast of the speed and smoothness with which triphenylmethylhydroxylamine rearranges under the influence of phosphorus pentachloride with the difficulty encountered in the case of its methyl derivative, emphasizes the great hindering influence of the methyl group. In this respect the result agrees with the observations made on benzoylphenylhydroxylamine[2] $C_6H_5CO.N(C_6H)_5OH$, acylchloroalkylamines,[3] RCO.NCl(Alkyl) and recently by Miss Vosburgh[4] on triphenylmethylchloromethylamine, $(C_6H_5)_3C.NCl(CH_3)$: in all these cases the prevention of the rearrangement by this interference seems to be complete.

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[1] Identified after hydrolysis to triphenylcarbinol.

[2] Leech, This Journal, 35, 1072 (1913).

[3] The exceedingly poor yield makes repetition of the experiment on a much larger scale desirable.

We may consider, on the basis of the facts summarized in (2), that the *easiest path* to the rearrangement of the molecule into a more stable one, representing a more stable distribution of electrons, is over the univalent nitrogen derivatives $RCO.N<$, $R_3C.N<$, etc. But it seems now that there must[5] be a *second* path since the formation of a methylaniline derivative indicated in the work just discussed probably[6] cannot go over a simple alkylimide derivative. Of the various possibilities that present themselves, only the most important will be mentioned now.

(1) We may consider again a direct exchange of radicals, such as Beckmann assumed, to wit:

$$(C_6H_5)_3C.N(CH_3)OH \longrightarrow (C_6H_5)_2C(OH).N(C_6H_5)(CH_3) \longrightarrow (C_6H_5)_2CO + C_6H_5NHCH_3 \quad (12)$$

Such a view would still be subject to the objections formerly made against it—it leaves out of account such facts as the role of the rearranging reagents in this action and in *the whole list of analogous rearrangements*, the difficulty of rearranging alkyl derivatives, as compared with nonalkylated compounds, and the rearrangement of azides, in which an exchange seems impossible. But even if such an assumption should finally have to be accepted—which is not likely—it would not preclude the formation of rearranging univalent nitrogen derivatives, where such can be readily formed. Frequently analogous results are obtained by quite different paths (for instance in the formation of hydrochlorides of metal bases and in the formation of alkyl halides from alcohols by the action of halogen acids, a reaction which has all the earmarks of not being a simple ionic reaction).

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[1] See footnote 3, p. 283.

[2] Stieglitz and Higbee, *loc. cit.*

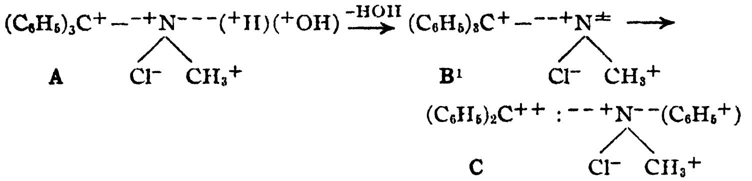
[3] Stieglitz and Slossen, *Ibid.*

[4] *Loc. cit.*

[5] In the discussions on pp. 276 and 281 it was only considered that there might be such a second, closely related path.

[6] See (3) below, in the text.

(2) The rearrangement of methyltriphenylmethylhydroxylamine may follow the course indicated for triphenylmethylhydroxylamine hydrochloride (Equation 8):



$$\underset{A}{(C_6H_5)_3C^+ - -\underset{Cl^- \quad CH_3^+}{{}^+N^-} - -({}^+H)({}^+OH)} \xrightarrow{-HOH} \underset{B^1}{(C_6H_5)_3C^+ - - -\underset{Cl^- \quad CH_3^+}{{}^+N^{\pm}}} \longrightarrow$$

$$\underset{C}{(C_6H_5)_2C^{++} : - - \underset{Cl^- \quad CH_3^+}{{}^+N^-} - ({}^+C_6H_5^+)} \quad (13)$$

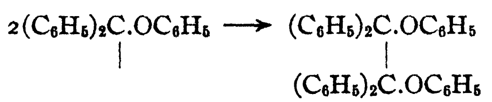
This represents the action as a rearrangement of a methyl chloride derivative **B** of triphenylmethylimide $(C_6H_5)_3C.N$. **B** would be an *electromer* of $(C_6H_5)_3C^+ - {}^-N^- {}^-({}^+Cl)({}^+CH_3)$, which has been prepared by Stieglitz and Vosburgh[2] and found *not* to rearrange. This view takes into account the action of the rearranging agent. It has been discussed in some detail above, and further experiments on its plausibility will be made.

(3) Phosphorus pentachloride might cause methyltriphenylmethylhydroxylamine to lose alcohol and form methyl chloride, which could subsequently methylate the aniline derivative formed by a primary rearrangement (Equation 6). In this event some of the phenylimidobenzophenone (Equation 6) should remain nonmethylated and aniline should be observed side by side with methylaniline. The hypochlorite tests gave no indication of its presence, but this possibility will also be further investigated.

(4) Wieland[3] has made the very interesting observation that triphenylmethylperoxide is decomposed by heat in the following way:

$$\underset{A}{(C_6H_5)_3C.O.O.C(C_6H_5)_3} \longrightarrow \underset{B}{2(C_6H_5)_3C.O—} \longrightarrow \underset{|\ C}{(C_6H_5)_2C.OC_6H_5} \quad (14)$$

and



$$2\underset{|}{(C_6H_5)_2C.OC_6H_5} \longrightarrow \begin{array}{c}(C_6H_5)_2C.OC_6H_5\\|\\(C_6H_5)_2C.OC_6H_5\end{array} \quad (15)$$

This rearrangement, which we shall call the "Wieland rearrangement," is, in its essential features, practically an exact parallel of the rearrangements of the nitrogen derivatives under discussion: we have univalent

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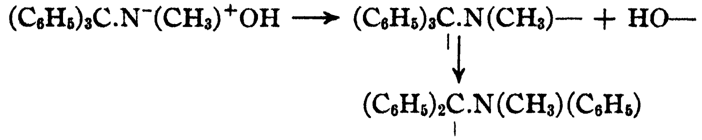
[1] See footnote [1], p. 280.

[2] The work will be published later.

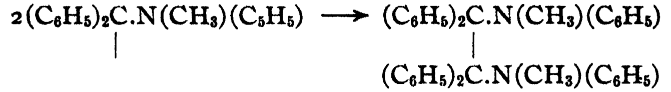
[3] *Ber.*, 44, 2550 (1911).

oxygen active (in B), in place of univalent nitrogen.[2] This suggests for the rearrangement of triphenylmethylhydroxylamine the following as a possible course:



$$\begin{array}{l} (C_6H_5)_3C.N^-(CH_3)^+OH \longrightarrow (C_6H_5)_3C.N(CH_3)— + HO— \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\quad (C_6H_5)_2\underset{|}{C}.N(CH_3)(C_6H_5) \end{array} \qquad (16)$$

and



$$2(C_6H_5)_2\underset{|}{C}.N(CH_3)(C_5H_5) \longrightarrow \begin{array}{l} (C_6H_5)_2C.N(CH_3)(C_6H_5) \\ \quad\;\; | \\ (C_6H_5)_2C.N(CH_3)(C_6H_5) \end{array} \qquad (17)$$

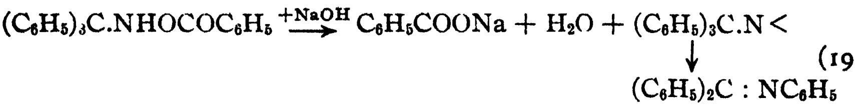
and

$$4HO— \longrightarrow 2HOH + O_2 \qquad (18)$$

Bivalent nitrogen in $(C_6H_5)_3C.N(CH_3)—$ would, in this case, be the cause of the rearrangement. The electron interpretation of this action would follow the same lines as laid down above. Mr. Stagner, who is continuing this work, will pay particular attention to this interesting possibility.[2]

The Rearrangement of Triphenylmethylbenzoylhydroxylamine.

The third problem raised in this investigation was on the behavior of benzoyltriphenylmethylhydroxylamine in reference to any rearrangement. Such a benzoyl derivative of triphenylmethylhydroxylamine was prepared (see the experimental part) and the product presumably has one of the following structures: $(C_6H_5)_3C.NHO.COC_6H_5$ or $(C_6H_5)_3C.N(COC_6H_5)OH$. The absence of any acid properties and of a ferric chloride reaction[3] rather favors the first structure given, the absence of hydrochloride formation favors the second structure and we consider the structure as undetermined. Which structure is correct is of less importance than the fact that the compound is found to undergo a rearrangement quite readily when it is heated with soda lime. We note at once the successful adaptation of the *reagent* to the compound to facilitate the primary loss of *benzoic acid* (sodium benzoate) in order to form the univalent nitrogen compound for the rearrangement. We may write:



$$\begin{array}{l} (C_6H_5)_3C.NHOCOC_6H_5 \xrightarrow{+NaOH} C_6H_5COONa + H_2O + (C_6H_5)_3C.N< \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (C_6H_5)_2C : NC_6H_5 \end{array} \qquad (19)$$

The Influence of Substitutions in the Aryl Groups.

The last question examined deals with the influence of substituting groups in determining which aryl radicals shall migrate from carbon to nitrogen in the rearrangement of triarylmethylhydroxylamines. It is a

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[1] See footnote 1, p. 281.

[2] Mr. Senior is investigating the behavior of the corresponding hydrazine derivatives.

[3] See experimental part.

very large problem and only a beginning has been made in it by the study of the action of phosphoric pentachloride on *p*-chlorotriphenylmethylhydroxylamine $(ClC_6H_4)(C_6H_5)_2C.NHOH$. The rearrangement occurs quite as readily as in the case of triphenylmethylhydroxylamine. Part of the substance forms phenylimidochlorobenzophenone

$$(ClC_6H_4)(C_6H_5)_2C.NHOH \xrightarrow{-HOH} (ClC_6H_4)(C_6H_5)_2C.N< \longrightarrow (ClC_6H_4)(C_6H_5)C : NC_6H_5 \qquad (20)$$

and another part forms *p*-chlorophenylimidobenzophenone:

$$(ClC_6H_4)(C_6H_5)_2C.N< \longrightarrow (C_6H_5)_2C : NC_6H_4Cl \qquad (21)$$

The quantitative examination of the reaction product showed, curiously enough, that roughly *two-thirds* of the substance rearranges according to the first action (equation 20), and one-third according to the second action: this represents a ratio which is also the ratio (2 : 1) of the number of phenyl to chlorophenyl radicals in chlorotriphenylmethylhydroxylamine, and such a result should follow if there were no particular effect at all of the halogen in the aryl radical on its likelihood to migrate to the nitrogen. A much larger experimental material will be needed before any final conclusions can be drawn as to such influences. It should, however, be further noted that Miss Vosburgh has obtained just *the same result* in examining the rearrangement of chlorotriphenylmethyldichloroamine $(ClC_6H_4)(C_6H_5)_2C.NCl_2$ by soda lime. It is evident that both the hydroxylamine derivative and the chloroamine

$$(ClC_6H_4)(C_6H_5)_2C.NCl_2 \xrightarrow{2NaOH} (ClC_6H_4)(C_6H_5)_2C.N< + NaCl + NaOCl + H_2O \qquad (22)$$

would form, according to our theory, exactly the same intermediate product $(ClC_6H_4)(C_6H_5)_2C.N<$. *Under the same conditions*, it should form identical products in the same proportions. In the present instance the temperature and other possibly vital conditions were quite different, and therefore too much emphasis must not be placed on the interesting result that identical products in the same proportions were actually obtained. The work, however, opens up a line of quantitative investigation which may lead to a means of applying quantitative tests of the validity of the theory.

Further studies along the lines indicated are in progress and it is hoped, in particular, that more light may be shed on the important questions of electromeric relations, which are so closely interwoven with the problem of the mechanism of these rearrangements.

NOTE.—In an important article in the December number of the *American Chemical Journal*, received today, Professor L. W. Jones develops more fully his views on the Beckmann and allied rearrangements and also contributes an interpretation of the rearrangements from the electron point of view. In two or three important details the views of the writer and of his colleague and friend are somewhat at variance. In the first place, the writer considers the oxygen in hydroxylamine and in oximes to have a positive charge and to be held by a negative charge on the nitrogen (although less stable electromers are not excluded)—Dr. Jones has assumed the oxygen to be negative and the nitrogen positive. The similar behavior of hydroxylamines and halogen amines, of hydroxylamine and hydrogen peroxide, still more the fundamental similarity existing between hydroxylamines and ammonia and between their salts, and, above all, the fact that, as far as the writer is aware, no hydroxylamine derivative has been found to exchange hydroxyl for halogen by treatment with halogen acids or phosphorus halides are the facts on which the writer's views are based. (According to a later private communication from Dr. J. he has now reached the same conclusion on this question and has discovered further evidence supporting it) In the next place, the writer considers that his original theory of "the potency of the free valences of univalent nitrogen" is in complete accord with the electronic expressions of this theory given by the writer and by Dr. Jones. In such univalent nitrogen derivatives, *e. g.*, RCO.N, it is not necessary to consider that the two free valences consist of a positive and a negative charge, though there will be a great, but not necessarily exclusive tendency toward the formation of such charges. In other words we would still distinguish between two closely related substances, easily convertible into each other, $RCO\,N<$ and $RCO.N\pm$. The distinction is an important one (cf Stieglitz and Curme, THIS JOURNAL, 35, 1146 (1913)) In the first substance only one of the three nitrogen valences is satisfied, the other two are present in the form of latent or potential valences, much as free metals like sodium or calcium have only latent or potential valences· exactly as we ascribe the tremendous activity of sodium to its tendency to throw off electrons and form sodium ion, so the activity of univalent nitrogen in effecting these rearrangements may well be due to the potency of the free or, in modern terms, latent valences of univalent nitrogen, *i e.*, to its great tendency to absorb, for each nitrogen atom, two electrons and go from $RCO.^{-}N<$ into $RCO.^{-}N^{=}$. On the other hand, we may also have, through the absorption of two electrons for each nitrogen atom, the transformation $RCO\,^{-}N\pm$, into $RCO.^{-}N^{-}$, corresponding to the transformation of Cl^{+} into Cl^{-} by the absorption of electrons We would leave the way open to either interpretation of the absorption of electrons, as more in accordance with the facts. This broader view of "the potency of the free valences of univalent nitrogen" is particularly emphasized because it enables the writer to include under the same theory not only all the rearrangements previously discussed by himself and so ably presented by Jones, but also the rearrangement of peroxides (the Wieland and other rearrangements) through the potency of univalent *oxygen* derivatives, the rearrangement of hydroxylamine derivatives RR'NOH possibly through *bivalent nitrogen* derivatives and the decomposition, by electrolysis, of organic acids. Finally, the writer believes that the explanation of the migration of a freed positive radical (see the text) to a negative atom under the influence of an electrical field of force gives an adequate explanation of the mechanism of the migration or "wandering," for which Professor Jones concludes that no satisfactory mechanism has, as yet, been offered. In regard, however, to the most fundamental questions of these rearrangements, considered from the electronic point of view, postulating a shifting of electrons from carbon to nitrogen, and a migration of a positive radical, Professor Jones and the writer are happily in entire agreement and the writer is glad to express here his great satisfaction thereat.—J. STIEGLITZ, *Jan. 10, 1914.*

Experimental Part.[1]

β-Triphenylmethylhydroxylamine $(C_6H_5)_3CNHOH$.[2]—The work on this compound was first undertaken by Stieglitz and Reddick[1] but not completed, therefore it was repeated. Triphenylmethylchloride was prepared according to Gomberg[2] and melted at 112–113°. For the preparation of β-triphenylmethylhydroxylamine, a modification of Mothwurf's[3] method was employed: A solution of sodium methylate was prepared by the addition of 7.3 grams of sodium to 100 cc. of acetone-free methyl alcohol. To this was added 19.5 grams of hydroxylamine hydrochloride, dissolved in methyl alcohol, and the precipitated sodium chloride was filtered off by suction. The hydroxylamine solution was evaporated, under reduced pressure, to 40–50 cc., and 10 grams of triphenylchloromethane, in about 25–30 cc. of benzene, were added. The methyl alcohol remaining was distilled over at ordinary pressure, but the benzene[4] was entirely removed by distillation under reduced pressure at about 70°. The dry residue was extracted with absolute ether, the solution filtered and the triphenylmethylhydroxylamine hydrochloride precipitated by dry hydrogen chloride gas. The salt was filtered, washed well with ether, and shaken in a separatory funnel with a layer of ether and dilute sodium hydroxide solution. The ether extract was drawn off, dried with fused calcium chloride, and the ether evaporated, leaving crystals of triphenylmethylhydroxylamine, melting at 130–135°. The yield was 73–75% of the theoretical.

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[1] The experimental part of this investigation was carried out by Dr. Leech and I wish to use this opportunity to acknowledge my grateful appreciation of his conscientious and skilful assistance.—J. Stieglitz.

[2] *Report of the VIII Internat. Congr. Appl. Chem.*, 25, 443 (1912).

Rearrangement of β-Triphenylmethylhydroxylamine with Phosphorus Pentachloride.—Triphenylmethylhydroxylamine (4 grams) was dissolved in absolute ether (about 40 cc.), and phosphorus pentachloride (4 grams) was added to the solution. The mixture was kept, under a reflux, at the boiling temperature of ether for twenty to thirty minutes. A yellow precipitate formed, which was filtered off and washed well with absolute ether. After the precipitate was dried and allowed to stand *in vacuo* over night, it melted at 187 189°, indicating it to be phenylimidobenzophenone hydrochloride, $(C_6H_5)_2C : NC_6H_5.HCl$. The yield was 4.1 grams or 96% of the theoretical. Upon hydrolysis of a small portion of this precipitate, the hypochlorite test for aniline was affirmative. Benzophenone was also identified by its melting point (47–50°) taken with the product itself and for a mixture (47–50°) of the product with pure benzophenone (melting point 48-52°). Further, for the liberation and identification of the free base, phenylimidobenzophenone, 3.3 grams of the hydrochloride was shaken in a separatory funnel with a concentrated solution of potassium carbonate and a layer of ether. The ether extract was dried over calcium chloride for one-half hour, and the ether allowed to evaporate spontaneously in a current of dry air in a bell jar desiccator. The residue was purified by treatment with ligroin. The yield was 2.2 grams and the melting point was 113°, agreeing with the melting point of phenylimidobenzophenone.

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[1] Peterson, P. P, *Am. Chem. J.*, 46, 327 (1911)

[2] *Ber.*, 33, 3147 (1900).

[3] *Ibid.*, 37, 3152 (1904).

[4] In the first experiments, the benzene was driven off at the temperature of boiling water, under ordinary pressure. An exceedingly severe explosion occurred once, and hence the modification to reduced pressure.

0.2911 gram substance gave 14.2 cc. N (over 33% KOH) at 21.5° and 747.5 mm. Calculated for $C_{19}H_{15}N$: 5.45% N. Found: 5.49% N.

Upon distillation of the original ether filtrate (after the treatment with phosphorus pentachloride) only a very small residuum remained after the phosphorus oxychloride had passed over.[1] These results completely identify the product of the action of phosphorus pentachloride on triphenylmethylhydroxylamine as phenylimidobenzophenone, formed by a molecular rearrangement according to:

$$(C_6H_5)_2C.NHOH + PCl_5 \longrightarrow (C_6H_5)_2C : NC_6H_5HCl + POCl_3 + HCl.$$

The hydrolysis of this product to aniline and benzophenone is expressed in the equation:

$$(C_6H_5)_2C : NC_6H_5HCl + HOH \longrightarrow (C_6H_5)_2C=O + C_6H_5NH_3Cl.$$

When triphenylmethylhydroxylamine is dissolved in phosphorus oxychloride and phosphorus pentachloride is added to the solution, the triphenylmethylhydroxylamine undergoes decomposition. Half a gram of the hydroxylamine derivative was dissolved in 5 cc. of phosphorus oxychloride and 0.5 g am of phosphorus pentachloride was added to the solution. After standing three days the mixture was poured on ice and the precipitate filtered off. The product gave the melting point of 155°, and after a portion of it was mixed with triphenylcarbinol (melting point of carbinol 159–161°) it melted at 157–159°. The yield was 98% of the theoretical. The filtrate reduced Fehling's solution, showing the presence of hydroxylamine.

Action of Beckmann's Mixture (Glacial Acteic Acid, Acetic Anhydride and Hydrogen Chloride), of Glacial Acetic Acid, and of Acetic Anhydride on Triphenylmethylhydroxylamine.—All attempts to effect a rearrangement of triphenylmethylhydroxylamine by means of the above agents failed, as the hydroxylamine derivative was decomposed. The reaction mixtures were poured on ice and in all cases triphenylcarbinol was found quantitatively, and the presence of hydroxylamine detected in the filtrate by reduction of Fehling's solution. Half a gram of triphenylmethylhydroxylamine was treated with 6 cc. of Beckmann's mixture (4 parts glacial acetic acid, 1 part acetic anhydride, saturated with dry hydrogen chloride) and allowed to stand three weeks. At the expiration of that time, quite a little triphenylmethylchloride had crystallized out of the solution and it was identified by its melting point, which remained unchanged when pure triphenylchlormethane was mixed with the product. The remaining triphenylmethylchloride, converted into triphenylcarbinol, was recovered in theoretical quantity. Hydroxylamine was detected as above.

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[1] In the older work with Mr. Reddick small quantities of triphenylcarbinol were occasionally identified when this residue was purified by treatment with aqueous alcohol. This result, indicating a slight decomposition of triphenylmethylhydroxylamine into triphenylmethylchloride, is parallel to the main action, the rearrangement into phenylimidobenzophenone. It is a product of some interest since we have found (see below) that in the treatment of the methylated derivative, $(C_6H_5)_3CN(CH_3)OH$, with phosphorus pentachloride, almost all the substance is decomposed in this way, forming triphenylmethylchloride, and only very small quantities are rearranged.

Action of Phosphorus Pentoxide on β-Triphenylmethylhydroxylamine-hydrochloride $(C_6H_5)_3CNH_2(OH)Cl$.—Triphenylmethylhydroxylamine hydrochloride was prepared from a solution of the free base in absolute ether by precipitation with dry hydrogen chloride. The salt was washed with absolute ether and dried *in vacuo*. The hydrochloride softens some at 143–147°, with change of form, and melts at 158–160°. It is soluble in alcohol, insoluble in cold water, ligroin or ether. Half a gram of the hydrochloride was intimately mixed with the same weight of phosphorus pentoxide in a test tube, and heated until a reaction took place.[1] The reaction mixture was then treated with a few drops of alcohol and some dilute hydrochloride acid water in order to hydrolyze any phenylimidobenzophenone formed. A little of this solution, made slightly alkaline with sodium hydroxide, gave upon the addition of bleaching powder solution, the purple color test for aniline, proving that a rearrangement to phenylimidobenzophenone had taken place. The remainder of the solution was shaken with ether, which removed the benzophenone and some acid. The aqueous solution was drawn off, the ether extract shaken with sodium hydroxide solution to remove the acid, the ether was separated and allowed to evaporate, leaving a residue which melted at 46–47°, the melting point of benzophenone. A melting point of a mixture of the product with synthetic benzophenone completed its identification as benzophenone, a product of the hydrolysis of phenylimidobenzophenone.

Triphenylmethylbenzoylhydroxylamine $(C_6H_5)_3C.N(COC_6H_5)OH$ or $(C_6H_5)_3C.NH(OCOC_6H_5)$.—Triphenylmethylhydroxylamine was dissolved in about forty times its weight of absolute ether and treated with benzoyl chloride, in the proportion of one molecule of the latter to two molecules of the former. The mixture stood from four to six days. A white precipitate formed, which was collected on a filter and found to consist chiefly of triphenylmethylhydroxylamine hydrochloride, with some benzoylated triphenylmethylhydroxylamine. The benzoyl derivative can be recovered by extraction of the precipitate with a very small amount of chloroform, and treatment of the extract with low boiling ligroin to precipitate the product fractionally. The original ether filtrate from the hydrochloride was allowed to evaporate in a current of dry air in a desiccator; the residue was washed with low boiling ligroin to remove benzoyl chloride, dissolved in a small amount of chloroform, and subsequently subjected to fractional precipitation with ligroin. After repeated fractionations a substance was obtained giving a constant melting point of 155°. The yield of pure substance was small.

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[1] The reaction proceeds rapidly at 75°.

0.2762 gram substance gave 9 7 cc N (over 33% KOH) at 18 8° and 736 5 mm.; 0.4963 gram substance gave 16 9 cc N (over 33% KOH) at 23 3° and 752 6 mm.; Calculated for $C_{26}H_{21}NO_2$· N, 3 70%. Found N, 3 94%, 3.83%.

Benzoyltriphenylmethylhydroxylamine is soluble in ether, chloroform and benzene. There are two possible structures for this benzoylated triphenylmethylhydroxylamine· the benzoyl group may have entered into the β-position of the hydroxylamine radical, forming $(C_6H_5)_3C.-N(COC_6H_5)OH$, or it may have entered the hydroxyl group (in the α-position), forming $(C_6H_5)_3CNH(OCOC_6H_5)$. The method of preparation corresponds to the one by means of which Beckmann[1] obtained β,β-benzoylbenzylhydroxylamine $(C_6H_5CO)(C_7H_7)N(OH)$ from β-benzylhydroxylamine and benzoyl chloride in an ether solution, and this makes the corresponding structure for our product probable. The latter did not, however, show the ferric chloride test (red coloration, characteristic of Beckmann's product) nor did it show any indications of acid (salt forming) properties at all. A hydrochloride of this compound could not be prepared by the usual method. This also agrees with Beckmann's failure to obtain a hydrochloride of β-benzoyl-β-benzylhydroxylamine. Attempts to obtain an isomeric α-benzoyl-β-triphenylmethylhydroxylamine, by the long and indirect process used by Beckmann[2] in preparing α-benzoyl-β-benzylhydroxylamine, were unsuccessful (see below). The exact position of the benzoyl group in our product therefore remains uncertain, though it most probably occupies the β-position.

Rearrangement of Triphenylmethylbenzoylhydroxylamine by Soda Lime.—Triphenylmethylbenzoylhydroxylamine (0.55 gram) was intimately mixed with pulverized soda lime (1 gram) and the mixture was heated in a test tube immersed in a metal bath, at 160–165°. At this temperature the rearrangement was found to proceed more favorably than at lower temperatures. The mixture became yellow, the color of phenylimidobenzophenone. The rearrangement product was extracted with a number of portions of benzene and the combined benzene extracts were evaporated in a current of dry air. A gummy residue was washed repeatedly with ligroin (b. p. 30–50°). A few yellow crystals were removed and identified as phenyliminobenzophenone by their melting point 108–110°. A mixture of the product with analyzed phenyliminobenzophenone (m. p. 113°) melted at 110–112°. The remainder of the phenylimidobenzophenone was then hydrolyzed by solution in 6–8 drops of alcohol and 2–3 cc. of dilute hydrochloric acid, and evaporation of the solution on a steam bath. Before the solution had become quite dry, cold water was added and a precipitate was removed by filtration. The precipitate was identified as benzophenone (0.21 gram). The filtrate was concentrated and chloroplatinic acid was added to it to precipitate aniline chloroplatinate which was identified by analysis.

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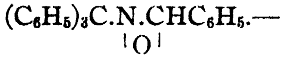
[1] *Ber.*, 26, 2283 (1893).

[2] *Loc. cit.*

0.2338 gram substance gave 0.0763 gram Pt. Calculated for $C_{12}H_{16}N_2PtCl_6$· 32.78% Pt. Found: 32.63% Pt.

Some doubt existing as to the exact structure of the benzoyl derivative of triphenylmethylhydroxylamine (see above), whose rearrangement has just been described, it was decided to attempt to prepare an isomeric benzoyl derivative by the method used by Beckmann for the preparation of α-benzoyl-β-benzylhydroxylamine.[1] The method, it will be recalled, is indirect, depending on the action of benzoyl chloride on the condensation product of benzyl hydroxylamine with benzaldehyde. The action of benzaldehyde on triphenylmethylhydroxylamine was, therefore, studied next.

Triphenylmethylhydroxylamine and Benzaldehyde,



$(C_6H_5)_3C.\underset{|O|}{N.CH}C_6H_5$.—

A small excess of triphenylmethylhydroxylamine (1.1 equivalent), was mixed with benzaldehyde in an Erlenmeyer flask, connected with a short reflux condenser. A small amount of absolute ether was added to the mixture, which was warmed for fifteen minutes at the temperature of boiling ether; the temperature was then slowly elevated, the ether being allowed to escape gradually, and a temperature of 120–140° was maintained for two hours. The resulting gum was successively triturated with small portions of low-boiling ligroin and the extracts collected until the sticky characteristic of the residue had been entirely removed and a nearly white powder produced. This powder consisted mostly of triphenylcarbinol. A sticky substance remained after the evaporation of the ligroin *in vacuo.* The solid was crushed on a clay plate, removed to a Hirsch funnel and washed a few times, without suction, with small amounts of cold absolute alcohol. The residue was then dissolved in a small amount of hot absolute alcohol and this solution separated from any insoluble portion by filtration. When the solution was allowed to cool slowly it deposited white crystals which were found to be the condensation product of benzaldehyde and triphenylmethylhydroxylamine. After a number of recrystallizations the condensation product melted at 114°.

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[1] *Loc. cit.*

0.4929 gram substance gave 17.8 cc. N (over 33% KOH) at 23.5° and 745.4 mm.; 0.1723 gram substance gave 0.5445 gram CO_2, 0.0975 gram H_2O. 0.1912 gram substance[1] gave 0.6028 gram CO_2, 0.1000 gram H_2O. Calculated for $C_{26}H_{21}NO$: 85.92% C; 5.78% H; 3.86% N. Found: 86.22, 86.00% C; 6.29%, 5.86% H; 4.02% N.

Triphenylmethylbenzaldoxime is soluble in ether, chloroform, benzene and hot alcohol, and not very soluble in ligroin. When it is dissolved in absolute ether and the solution is saturated with dry hydrogen chloride gas, the hydrochloride is precipitated quantitatively.

With the view of obtaining α-benzoyl-β-triphenylmethylhydroxylamine, benzaldehyde-triphenylmethylhydroxylamine was dissolved in absolute ether and treated with an equivalent quantity of benzoyl chloride. The mixture was allowed to stand for twenty-four hours and subsequently treated, as described by Beckmann in the preparation of α-benzoyl-β-benzyl-hydroxylamine. After repeated attempts, all of which yielded negative results, the project was abandoned.

Parachlorophenyldiphenylmethylhydroxylamine, $(ClC_6H_4)(C_6H_5)_2CNH(OH)$.—Parachlorophenyldiphenylmethylchloride was prepared by Gomberg's[2] method from benzophenonedichloride and chlorobenzene with the aid of the Friedel and Craft's reaction. The chloride was generally recrystallized four or five times from hot ligroin (b. p. 70–80°) and melted at 88–88.5°. Gomberg gives 87° as its melting point. The chloride was condensed with hydroxylamine by a modification of Mothwurf's method as follows: Hydroxylaminehydrochloride (2.8 grams) was dissolved in the least amount of methyl alcohol possible and to it was added a solution of sodium methylate (0.91 gram sodium in 14 cc. alcohol). The precipitated sodium chloride was removed by rapid filtration, and the hydroxylamine solution treated with five grams of *p*-chlorophenyldiphenylmethylchloride in 50 cc. of benzene. The mixture stood for a number of hours, during which time a precipitate of hydroxylamine hydrochloride formed, but this was not removed. After the methyl alcohol had been evaporated, the benzene was removed by distillation under reduced pressures, at a temperature of 65–70°, until a "gummy dry" residue remained. This was extracted with dry ether, the hydroxylamine hydrochloride removed by filtration. An ether solution of pure anhydrous oxalic acid was added to the filtrate until no further precipitation occurred. The oxalate was collected on a filter, washed with ether by suction, and shaken in a separatory funnel with a solution of potassium hydroxide and an ether layer. The ether extract of the free base was dried with potassium carbonate; upon evaporation of the ether a gum resulted. This gum was transferred to a beaker by means of a little alcohol and placed in a desiccator *in vacuo*. Care must be taken to add alcohol, or else the substance will form a taffy-like foam, spreading over the entire vessel. After some time, generally twelve to eighteen hours, the gum changed to a solid. The yield of crude material was about 65–70% of the theoretical.

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[1] This was some of the unchanged substance recovered after treatment with benzoyl chloride (see next section); it was identified by its melting point, which was unchanged when the melting point of a mixture with a previously analyzed sample was taken.

[2] *Ber.*, 37, 1634 (1904).

The pulverized substance was treated with the smallest amount of ligroin (b. p. 70–80°) necessary to dissolve it, and the solution allowed to stand over night. In this manner a good part of the substance precipitated out and most of the gummy matter remained in solution. The precipitate was collected on a filter and washed with low-boiling ligroin; after this operation the product was dissolved in a small amount of benzene, four to six volumes of low-boiling ligroin were added to the solution, and the beaker, with contents, immersed in ice water for fifteen minutes. The precipitate of quite impure chlorophenyldiphenylmethylhydroxylamine, thus formed, was brought on a filter and the filtrate allowed to evaporate spontaneously in the air until the volume was about one-third the original one, crystals being deposited in this process. The remaining solution was then decanted into another vessel and the crystals, adhering to the sides of the beaker, were washed with ligroin (b. p. 30–50°). They were then dissolved in the least amount of hot ligroin[1] (b. p. 70–80°). After the solution had stood twelve hours the crop of new crystals was removed. One or two more recrystallizations completed the purification of the compound. The melting point is 117°. The yield was 25–30° of the theoretical.

0.1796 gram substance gave 0.4874 gram CO_2 and 0.0845 gram H_2O. Calculated for $C_{19}H_{16}NOCl$: C, 73.62%; H, 5.20%. Found. C, 74.01%, H, 5.27%.

Parachlorophenyldiphenylmethylhydroxylamine is soluble in ether, benzene, chloroform and hot high-boiling ligroin. If it is dissolved in absolute ether and dry hydrogen chloride gas is passed into the solution, the hydrochloride is thrown down. This salt is soluble in alcohol, insoluble in ether, ligroin and cold water; it is decomposed by warm water, probably into chlorophenyldiphenylcarbinol and hydroxylamine.

Rearrangement of Parachlorophenyldiphenylmethylhydroxylamine by Phosphorus Pentachloride.—In a round bottom flask, 0.5 gram of the hydroxylamine derivative was dissolved in 30 cc. of absolute ether, 0.5 gram of phosphorus pentachloride was added to the solution, and the flask was connected with a reflux condenser. The entrance of moisture was guarded against. The mixture was heated on an electric oven for two hours, during which time a yellow precipitate had collected in the flask. The precipitate was collected, washed well with ether and dried *in vacuo*. Upon evaporation of the filtrate, and subsequent distillation of the phosphorus oxychloride produced in the action, only one drop of residue remained. The yellow precipitate consisted of a mixture of *p*-chlorophenyldimidobenzophenone and phenylimido-*p*-chlorobenzophenone (see below). The salts were immediately hydrolyzed by solution in a few drops of alcohol and treatment with a small amount of very dilute hydrochloric acid, the mixture being heated about fifteen minutes to assure complete hydrolysis of the imido compounds. The ketones were extracted in the usual manner with ether, and the aqueous solution (see A) was examined for aniline and parachloraniline.

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[1] One part alcohol and three parts ligroin also serves as a good crystallizing solvent.

A. *Identification of Aniline and Parachloroaniline.*—The aqueous acid solution was placed in a small separatory funnel, strong caustic soda solution was added, and the free bases were extracted with ether. The ether extract was dried well with potassium carbonate and an ether solution of anhydrous oxalic acid[1] added to precipitate the oxalates of the two anilines. The precipitate was collected, washed well with absolute ether, transferred to a test tube and dissolved in the least amount of almost boiling water. Upon cooling the solution to about 40°, a precipitate again formed (*p*-chloroaniline oxalate), which was collected. The filtrate from it was made alkaline and gave with bleaching powder solution the characteristic test, proving the presence of aniline. The precipitate, consisting mostly of chloroaniline oxalate, and a small amount of aniline oxalate, was treated in a small dropping funnel, with alkali, and the mixture shaken with ether. After the ether solution had been dried it was allowed to evaporate spontaneously, and the residue placed in a vacuum desiccator. In a few hours crystals of *p*-chloroaniline appeared. These were washed quickly with ligroin, to remove any aniline present, dried, and melted at 65°. A melting point (68–69°) of a mixture of the product with pure parachloroaniline (70°) was identified the substance as *p*-chloroaniline.

B. *Identification of Benzophenone and Chlorobenzophenone.*—The ether solution containing the ketones, was spontaneously evaporated and the residue washed quickly with ligroin. Enough alcohol[2] was added to the residue just to dissolve about three-quarters to seven-eighths of it; the residue was collected and melted at 73–75°. *p*-Chlorobenzophenone melts at 77–78° and a mixture of the product with some synthetic substance melted at 75–77°, proving the identity of the product. The alcoholic filtrate was allowed to evaporate spontaneously to a very small volume, the solution filtered through a cotton plug, and the filtrate evaporated to dryness. The residue was then treated with ten to fifteen drops of alcohol, the solution decanted through a cotton filter, the filtrate evaporated almost to dryness, the remaining few drops of liquid once decanted from a small solid residue, which when dried, melted at 48–50°. Benzophenone melts at 48–52°.

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[1] The oxalic acid salts were prepared because of the greater relative solubility in water of the aniline salt than that of α-chloroaniline. The accuracy of the method of separation based on this difference was, of course, first tested and proved by preliminary experiments with known materials.

[2] Benzophenone is very soluble in alcohol, while *p*-chlorobenzophenone is less soluble.

A quantitative study of the rearrangement of *p*-chlorophenyldiphenylmethylhydroxylamine with phosphorus pentachloride was next made, in order to determine the proportions in which the rearrangement yields an aniline and a *p*-chloroaniline derivative. The hydroxylamine (0.85 gram) was dissolved in 30 cc. of absolute ether, and heated on the electric bath, as described above, with a gram of phosphorus pentachloride. After two hours the yellow precipitate was collected, washed well, with absolute ether, and then hydrolyzed in the usual manner. The ketones were removed by extraction with ether. The aqueous solution was then saturated with sodium chloride, placed in a small separatory funnel, made alkaline with strong sodium hydroxide solution and the two anilines twice extracted. The collected ether extracts were poured through a cotton filter and the solution dried with potassium carbonate. It was filtered into a beaker and the hydrochlorides of the anilines were precipitated by a freshly made ether solution of dry hydrogen chloride.[1] The salts were brought on a filter, well washed and dried; they weighed 0.212 gram.

A weighed portion of the chlorides was analyzed volumetrically for aniline and chloroaniline by the bromination method.[2]

0.0712 gram of the mixed hydrochlorides required 27.8 cc of $N/10$ $KBrO_3$ Found: aniline hydrochloride, 66.9%; chloroaniline hydrochloride, 33.1%.

In order to run analyses of other hydrochloride samples, two more rearrangements were made as above. The results of the bromination determinations were as follows:

0.0674 gram of the mixed hydrochlorides required 25.8 cc. of $N/10$ $KBrO_3$ Found: aniline hydrochloride 63.4%; chloroaniline hydrochloride, 36.6%, 0.0625 gram of the mixed hydrochlorides required 24.45 cc. of $N/10$ $KBrO_3$. Found: aniline hydrochloride, 67.3%; chloroaniline hydrochloride, 32.7%.

No greater degree of accuracy than 5% was aimed at in these results.

β,β-Triphenylmethylmethylhydroxylamine, $[(C_6H_5)_3C.N(CH_3)OH]$.—This compound was prepared by the action of triphenylmethylchloride on methylhydroxylamine hydrochloride. The β-methylhydroxylaminehydrochloride was prepared by a series of preparations, all of which are described in the literature.[3]

β-Methylhydroxylaminehydrochloride (2.5 equivalents) was dissolved in ten times its weight of methyl alcohol (acetone free) and a solution of sodium methylate, prepared from an equivalent weight of sodium dissolved in another equal volume of methyl alcohol, was poured into the hydroxylamine solution, which operation, after the flask had been shaken, was quickly followed by the addition of triphenylmethylchloride (one equivalent), dissolved in 30–40 times its weight of dry benzene. The reaction mixture generally stood over night, though more or less time can be allowed. The precipitates of sodium chloride and methylhydroxylamine hydrochloride were not removed from the liquid, but the contents evaporated, under reduced pressures, to a gummy dryness and the residue extracted with dry ether and the extract filtered. To the filtrate, with vigorous stirring, a saturated ether solution of dry hydrogen chloride was added, the precipitate was collected and washed well with ether.[1] The hydrochloride was then dissolved in the least amount of chloroform, and again precipitated with absolute ether, to which a few drops of ethereal hydrogen chloride was added. This process was once more repeated. The purified hydrochloride was shaken with an ether layer and a fairly strong solution of potassium hydroxide, the ether extract, after separation, dried with calcium chloride, and the ether evaporated. It left a gum. This gum was transferred, with the aid of a little alcohol, to a beaker, which, with contents, was placed in a bell jar[2] *in vacuo*. After standing some time, and with frequent rubbing, solidification took place. The solid was washed with ligroin (b. p. 30–50°), dissolved in hot ligroin (b. p. 70–80°). After this solution had cooled an equal volume of low-boiling ligroin was added to it. The solution was allowed to evaporate very slowly, spontaneously, small crystals forming upon the walls of the vessel. These were removed and the recrystallization repeated, until a constant melting point of 113° was obtained for the compound.

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[1] Experiments showed that hydrogen chloride precipitates aniline and chloroaniline quantitatively as hydrochloride from a dry ether solution.

[2] See Curme, THIS JOURNAL, **35**, 1143 (1913).

[3] Beckmann, *Ber.*, **20**, 1509, 2766 (1887); **22**, 432 (1889); **23**, 1685 (1890); Dittrick, *Ber.*, **23**, 3548 (1890). We found it better to use methyl bromide rather than the iodide.

0.1695 gram substance gave 0.5156 gram CO_2 and 0.1001 gram H_2O. Calculated for $C_{20}H_{19}NO$: C, 82.99%; H, 6.63%. Found: C, 82.95%; H, 6.64%.

β-Triphenylmethyl-β-methylhydroxylamine is soluble in alcohol, benzene, chloroform, ether and hot ligroin. When it is heated with aqueous hydrochloride acid, it is hydrolyzed, forming triphenylcarbinol and methylhydroxylamine hydrochloride.

The Action of Phosphorus Pentachloride on β,β-Triphenylmethylmethylhydroxylamine.—One gram of the hydroxylamine was placed in a round bottom flask with 10–12 cc. of absolute ether and one gram of pure phosphorus pentachloride was added to the solution. The flask, frequently rotated, was heated for four hours, the boiling ether being refluxed by a condenser, care having been taken that no moisture could enter. A yellowish white precipitate[1] resulted, which was brought on a filter and washed well. (For the examination of the filtrate "F" see later.) The precipitate was treated with 6 cc. of acidulated cold water in which it all dissolved. A drop or so of the solution reduced a correspondingly small amount of Fehling's solution, indicating the presence of methylhydroxylamine. The aqueous solution was placed in a separatory funnel, saturated with sodium chloride, made alkaline with strong sodium hydroxide solution and shaken with absolute ether. The alkaline solution was drawn off (it gave forth the odor of methylhydroxylamine), the ether extract poured through a cotton filter separatory funnel, and shaken with a solution of one cc. of N/HCl in five cc. of water. The aqueous extract was drawn off, and delivered through a cotton filter into a weighed beaker. The ether was again treated as above and the second aqueous extract combined with the previous one. The hydrochloric acid solution was evaporated in a desiccator to dryness, leaving a residue weighing 0.0672 gram. The residue was partly crystalline, partly oily. Upon evaporation of the ether, no residue remained.

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[1] Oxalic acid, in ether solution, will not cause a precipitate.

[2] If paraffin shavings are present in the jar, the solidification seems to take place sooner.

A small portion of the solid residue was dissolved in water and made slightly alkaline with sodium hydroxide. Part of this solution was tested with a half-saturated solution of bleaching powder and gave no test for aniline, but with a very small amount of calcium oxychloride solution it gave the very delicate and characteristic test,[2] a navy blue fading into yellow, for monomethyl or monoethyl aniline. Another portion of the solution, neutralized, gave a small amount of yellow oil (nitro-nitrosomethylaniline), with nitrogen trioxide, and when the mixture was heated it did not smell of nitrophenol, again assuring the absence of aniline. In order to determine positively whether methyl- or ethyl-aniline was present, it was decided to convert the base into its acetyl derivative. The remaining portion of the solid in the beaker was dissolved in $^1/_2$ cc. of water, the beaker rinsed with $1^1/_2$ cc. of strong potassium hydroxide solution into a weighing bottle, and to the strong alkaline mixture, a large excess of acetylchloride was added in small portions, with vigorous shaking of the bottle. After standing some time, the solution was shaken with ether in a separatory funnel, the ether drawn off, and evaporated, and the residue crystallized out of ligroin. Crystals melting at 95.5° were obtained. Some synthetic methyl-acetanilide[3] melted at 101–102°; a mixture of the compound melting at 95.5° and some pure methyl-acetanilide melted at 99.5–100°, thus indicating the identity of the two.

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[1] If the mixture is heated for only a short time, twenty to thirty minutes, which is amply sufficient for the rearrangement of phenylmethylhydroxylamine, one recovers quite a large proportion of the hydrochloride.

[2] Leech, THIS JOURNAL, 35, 1042 (1913).

[3] Hofmann, *Ber.*, 7, 523 (1874); Leech, *loc. cit.*

Only a few milligrams of the methylacetanilide[1] were obtained. After saponification of the methylacetanilide with boiling hydrochloric acid, the solution was made alkaline; the addition of calcium hypochlorite again gave the methylaniline test.

The original ether filtrate, "F" obtained in the treatment of triphenylmethylmethylhydroxylamine with phosphorus pentachloride, was placed in a separatory funnel and shaken with an alkaline solution. After separation of the ether, and on evaporation of the latter, a residue remained, which was identified as triphenylcarbinol by its melting point and its behavior when the melting point of a mixture of the product and pure carbinol was taken. Its weight was 0.68 gram, or 75% of the theoretical for a complete decomposition of triphenylmethylmethylhydroxylamine by phosphorus pentachloride, into triphenylmethylchloride.

The Action of Phosphorus Oxychloride and Phosphorus Pentachloride on β-Triphenylmethyl-β-methylhydroxylamine.—Half a gram of the hydroxylamine derivative was dissolved in 6 cc. of phosphorus oxychloride, to which was added half a gram of phosphorus pentachloride; the mixture was allowed to stand three or four days. The solution was then poured on crushed ice and the precipitate filtered off and dried. It was identified as triphenylcarbinol. The yield was quantitative. The filtrate reduced Fehling's solution and after being made alkaline, it gave the characteristic odor of methylhydroxylamine.

The Action of Beckmann's Mixture on β,β-Triphenylmethylmethylhydroxylamine.—Half a gram of the hydroxylamine derivative was dissolved in 6 cc. of Beckmann's mixture, and allowed to stand a week. As in the previous case, the mixture was poured on ice, the precipitate filtered off and identified as triphenylcarbinol. The yield was quantitative. The filtrate reduced Fehling's solution, and upon treatment with alkali it gave methylhydroxylamine which was detected by its odor.

The Action of Phosphorus Pentoxide on β,β-Triphenylmethylmethylhydroxylamine Hydrochloride.—Pure triphenylmethylmethylhydroxylamine was dissolved in absolute ether, a solution of hydrogen chloride in ether was added to it, and the precipitate that formed was collected. β,β-Triphenylmethylmethylhydroxylaminehydrochloride melts at 102°, and is soluble in alcohol and chloroform; insoluble in ether, ligroin, and cold water.

Half a gram of the hydrochloride salt was intimately mixed, in a test tube, with half a gram of phosphorus pentoxide, the mixture heated a few minutes in the free flame until no further action was apparent. The contents were treated with a few drops of alcohol, hydrolyzed with acidulated water, transferred to a separatory funnel and shaken with ether.

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[1] This method of acetylation, if care is taken, produces yields of 90–95% of the theoretical, as was ascertained with pure methylaniline.

The ether extract was separated, evaporated, and the residue upon purification identified as triphenylcarbinol. The acid aqueous solution was placed in a separatory funnel, made alkaline, and shaken with ether. The aqueous extract was drawn off and soon smelled of methylhydroxylamine. The ether extract was shaken with a solution of one cc. of N/HCl in 5 cc. water, the acid extract was drawn off, and after having been made slightly alkaline, the addition of bleaching powder solution gave no test for methylaniline or aniline.

CHICAGO, ILL

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE]

OCTOIODOPARAQUINHYDRONE.[1]

BY C LORING JACKSON AND E K BOLTON

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The work described in this paper grew out of the suggestion of the late Professor H. A. Torrey that one of us (Bolton) should take up the study of iodoanil, begun by him and Dr. Hunter.[2] After the too early death of Professor Torrey the research was continued by us, and among other derivatives of iodoanil, the description of which will appear soon in another paper, we tried to make the corresponding octoiodoquinhydrone. For this purpose we exposed a benzene solution of iodoanil to the action of sulfurous acid at ordinary temperatures and, after four weeks, were rewarded by the appearance of glistening black crystals of considerable size. These differed in color from crystals of iodoanil (prepared from benzene for the sake of comparison), as the latter were brown, but both formed flattened prisms or long plates terminated by two planes at an obtuse angle, and, although slight differences appeared, they seemed to us more in habit than real crystalline form. It was therefore necessary to bring convincing proofs that these black crystals were not iodoanil but a new substance, and we think, these will be found in the following observations: Treatment of the black crystals with benzene and alcohol, toluene, or glacial acetic acid yielded in each case a yellow solution, from which, in addition to the brown crystals of iodoanil, a quantity of a white substance soluble in sodium hydroxide was obtained, which can hardly be anything but tetraiodohydroquinone. An aqueous solution of sodium hydroxide disintegrated the crystals, leaving a brown powder (iodoanil), and dissolving a white substance (tetraiodohydroquinone). Parallel experiments with iodoanil showed that the alkaline solution was without action under the same conditions, and that the organic solvents yielded only brown crystals with no white admixture whatever. The crystals have therefore behaved like the quinhydrone which should be dissociated by solvents[1] or decomposed by sodium hydroxide into iodoanil and tetraiodohydroquinone.

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Elmer Keiser Bolton.

[2] THIS JOURNAL, 34, 702 (1912).

A quantity of iodoanil was dissolved in benzene and submitted to the action of sulfurous acid at ordinary temperatures. The amount of solid in 50 cc. was determined at the beginning of the experiment, and again after the black crystals had been formed. The second determination yielded 0.1362 gram less solid than the first, showing that a substance less soluble than iodoanil had been formed and precipitated. The experiment was carried on in a tightly corked flask, the weight of which remained constant during the formation of the crystals. This seems to us an absolute proof that the black crystals are not iodoanil.

The behavior of the black crystals, when heated, also leads to the same conclusion, for they began to decompose at 190° with evolution of iodine, and did not melt even at much higher temperatures; whereas the iodoanil, from which the black crystals were obtained, began to soften at 260°, and melted at 265° with decomposition but no evolution of iodine.

The black crystals contained the amount of iodine required by the octoiodoquinhydrone, but the analysis has little significance, because iodoanil, or tetraiodohydroquinone, contains essentially the same percentage.

Although the quinhydrone could be prepared by the method described above and also by the action of iodoanil and tetraiodohydroquinone on each other in benzene solution, the yield was never large, and occasionally no reaction took place, so that it seems as if the two substances have but a slight tendency to combine to make the quinhydrone. But its formation, at all, is of interest, because it is the first paraquinhydrone containing 8 atoms of halogen which has been obtained. Staedeler,[2] it is true, thought that he made the octochloroquinhydrone by the action of ferric chloride, or nitric acid, on tetrachlorohydroquinone, but his product was yellow, and, therefore, could not have been the quinhydrone. The early date of this work (1849) accounts for his ignorance of the fact that a dark color is the essential character of these bodies. Our real knowledge of this subject is due to the thorough work of Ling and Baker,[3] who tried to prepare a quinhydrone from chloroanil under the most varied conditions, but without a sign of success, except when they boiled for 3 hours a xylene solution of chloroanil and tetrachlorohydroquinone and obtained dark violet prismatic needles; but in spite of the resemblance of these crystals to a quinhydrone, they proved that they were tetrachlorohydroquinone, colored by some impurity, since a quantitative oxidation gave results corresponding to this substance. They are of the opinion that the color is due to a trace of a quinhydrone, but one containing less than 8 atoms of chlorine, as this result was obtained with xylene purified only by distillation, which might contain some reducing impurity, while on repeating the experiment with xylene purified with sulfuric acid no dark color was observed. Ling and Baker's paper therefore establishes the fact that the octochloroquinhydrone is not formed under conditions which give quinhydrones easily with substances containing less halogen, so that, if it can exist at all, for which there is no evidence, it must be a very unstable compound. This conclusion is supported by an experiment of our own, in which chloroanil was exposed to the conditions, which had yielded the octoiodoquinhydrone, but there was no evidence whatever that any reaction had taken place; and a similar experiment with bromoanil gave the same result. So far as we have found, no other experiments have been tried with bromoanil, and, although this one indicates that like chloroanil it resists vigorously the formation of a quinhydrone, many more under varying conditions are needed before this property of bromoanil can be considered definitely established.

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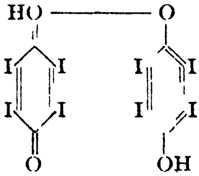
[1] Torrey and Hardenbergh, *Am. Chem. J.*, 33, 167 (1905).

[2] *Ann.*, 69, 329 (1849).

[3] *J. Chem. Soc.*, 63, 1323 (1893).

Richter[1] has proposed a theory for the constitution of the quinhydrones, according to which they are oxonium salts, so that our compound would have the formula



and he has pointed out that the difficulty in forming octohalogen quinhydrones was to be expected, since the negative radicals would reduce the basic character of the oxygen, on which the formation of the oxonium salt depends. Our discovery of an iodine compound, when those with chlorine and perhaps bromine could not be obtained, is certainly in harmony with this theory, as the less negative iodine would interfere with the formation of the oxonium salt less than either chlorine or bromine, but we cannot see that the other structural formulas proposed[2] for the quinhydrones would explain our observations.

The difficulty in forming octohalogenquinhydrones does not appear in the ortho series, as the tetrachloro-[3] or tetrabromoorthoquinone[4] forms

[1] *Ber.*, 43, 3603 (1910).

[2] Jackson Oenslager, *Am. Chem. J.*, 18, 1 (1896); Valeur, *Ann. chim. phys.*, 21, 470 (1900); Posner, *Ann.*, 336, 85 (1904); Urban, *Monatsh.*, 28, 299 (1907); Willstätter, *Ber.*, 41, 1464 (1908).

[3] Jackson and P. W. Carleton, *Am. Chem. J.*, 39, 493 (1908).

[4] Jackson, Russe, *Ibid.*, 35, 174 (1906).

such a compound under varied conditions and with large yields. If the negative influence of the halogen is the only thing which stands in the way of the quinhydrone formation, this difference must be due to the differences in position of the halogen in the ortho and paraquinones. In trying to discover the effects of halogens in certain positions on basicity, we naturally turned to the halogen amino compounds, and were astonished at the meagerness of the material available. The two dibromoanilines, 1,2,6 and 1,2,4, were the only compounds known which seemed to us to furnish a serviceable analogy with the tetrahalogen para- and orthoquinones. The hydrochloride of the 2,6 compound[1] loses the acid easily by standing, in the air, and is decomposed by water. The 2,4 compound,[2] on the other hand, forms stable salts, which can be recrystallized. The inference from these observations is that the diorthohalogen (occurring in the paraquinone) has a greater influence on the basicity than the orthoparahalogen (as in the orthoquinone), and, while we find no entirely satisfactory confirmation of this view among the other known halogen amino compounds, there is certainly nothing opposed to it. In this single case, therefore, we have phenomena similar to those observed with para- and orthoquinones, if the quinhydrones are oxonium salts.

In the discussion given above it was assumed that the presence of halogens is the only condition which influences the formation of the quinhydrones, but it is probable that this is not the case. The mutual action of the two atoms of oxygen, for instance, might have a considerable effect on their tendency to form oxonium salts. So far as we know there are no data sufficient to decide this question; but the fact that chloroanilic acid forms a quinhydrone easily[3] may indicate that the presence of two atoms of oxygen in the ortho position is favorable to the formation of these bodies, although in this case only one of them is quino oxygen. Here, then, may be another reason for the formation of the octohalogen orthoquinhydrones.

Torrey and Hunter[4] give reasons for believing that the green compounds obtained by them from tetrachloro- or tetrabromoquinone, whether para or ortho, and potassium or sodium iodide in acetone, are salts of octohalogen quinhydrones. If this view is correct, it is necessary to explain the formation of a salt of a quinhydrone, which cannot exist in the free state. They suppose it depends on the solubility, assuming that the octochloroquinhydrone is soluble, because Ling and Baker[5] found that the solubility of their quinhydrones increased with the amount of chlorine they contained. The soluble quinhydrone, therefore, would not

[1] Heinichen, *Ann.*, 253, 275 (1889).

[2] Hofman, *Ibid.*, 53, 47 (1845).

[3] Graebe, *Ibid.*, 146, 36.

[4] THIS JOURNAL, 34, 702 (1912).

[5] *J. Chem. Soc.*, 63, 1314 (1893).

be formed, while the nearly insoluble salt would be precipitated. Our observation that the octoiodoquinhydrone is nearly insoluble seems to us to remove the foundation of this hypothesis. We cannot, however, find one to replace it, unless, indeed, we guess that the presence of the sodium may reduce the negative effect of the eight chlorine atoms sufficiently to allow the formation of the oxonium salt.

Preparation of Iodoanil.

The bromoanil necessary for this work was prepared by a modification of Ling's method,[1] as follows: 50 grams of hydroquinone suspended in 300 cc. of glacial acetic acid were treated with 400 grams of bromine, followed by an excess of nitric acid of specific gravity, 1.42, and the mixture was heated gently. The product was pure enough to be converted directly into iodoanil.

The method for making the iodoanil differed in some particulars from that of Torrey and Hunter.[2] Twenty-five grams of bromoanil mixed with 23 grams of potassium iodide and 250 cc. of alcohol were heated on the steam bath under a reverse condenser for two hours. The reddish brown diiododibromoquinone obtained in this way, after being washed with water and alcohol, was returned to the flask and was heated again for two hours with 20 grams more of potassium iodide. The iodoanil formed was pure after two crystallizations from benzene, as shown by the following analyses:

0.2362 and 0.1927 g. subst. gave 0 3618 and 0.2965 g. AgI; calc. for $C_6I_4O_2$, 83.01% I; found, 82.80 and 83.18%.

The principal advantage of this method over that of Torrey and Hunter is the substitution of the much cheaper potassium iodide for sodium iodide in the second stage of the process, and the use of larger quantities of bromoanil. They found that poor yields were obtained with quantities larger than 15 grams, while with our modifications the process gave good results with as much as 50 grams, both as to quantity of yield and quality of product.

Octoiodoparabenzoquinhydrone.

Two grams of iodoanil (purified by one crystallization from benzene) were dissolved in 125 cc. of benzene, and after the addition of three drops of water the solution was completely saturated with sulfurous dioxide. It was then allowed to stand in a tightly corked flask at ordinary temperatures. At the end of three weeks there was no apparent change, the solution being still clear and dark red; but after the fourth week a considerable quantity of black shining crystals had been deposited, which were filtered out, washed several times with benzene, and dried *in vacuo*.

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[1] *J. Chem. Soc.*, 61, 568 (1892).

[2] THIS JOURNAL, 34, 708 (1912).

0.2864 g. subst. gave 0.4370 g. AgI; calc. for $C_6I_4O_2C_6I_4(OH)_2$, 82.86% I; found, 82.50%.

A parallel analysis confirmed this, but owing to an accident gave a still lower percentage.

Properties of Octoiodoparabenzoquinhydrone.—The substance was deposited from the benzene solution used in its preparation in narrow plates, or flat prisms, terminated often at both ends with two planes at an obtuse angle. Iodoanil, crystallized from benzene under similar conditions for the sake of comparison, appeared in similar long plates but narrower than those of the quinhydrone, and although one end was terminated by two planes at an obtuse angle, the other, when well developed, was bounded by a single plane at right angles to the sides. It was also harder to obtain large crystals from the iodoanil than from the quinhydrone. All these differences, however, while apparently constant, seemed to us more like differences in habit than in crystalline form. The quinhydrone is black with a metallic reflex and a brilliant luster, the iodoanil brown. In experiments similar to that described above, in which the moist benzene solution of iodoanil, after saturation with sulfurous dioxide, was allowed to evaporate slowly in an open flask instead of being tightly corked, some of the resulting crystals were brown and others black, although of the same size and thickness; and this difference was so marked that it could be used for distinguishing between the quinone and the quinhydrone.

The crystals of the octoiodoquinhydrone were permanent in the air, and when heated to 100° showed no loss in weight, or change of appearance. At 190° they began to decompose with evolution of violet vapors of iodine, and this decomposition continued, as the temperature rose, but the substance did not melt even at 265°. A parallel observation made at the same time showed that the iodoanil, from which the sample of quinhydrone was obtained, began to sinter at 260°, and was completely melted at 265°, the fusion being accompanied by decomposition but without evolution of iodine vapor.

The octoiodoquinhydrone is a very slightly soluble compound, being practically insoluble in alcohol, ether, chloroform, ethyl acetate, benzene, toluene, glacial acetic acid, or carbon disulfide, and slightly soluble in acetone, when the solvent is cold, but it is fairly soluble in any of these liquids if it is hot. In each case the solution was yellow, and the striking change from the black solid to the yellow solution suggested that the quinhydrone had dissociated. To study its behavior in this respect a quantity was dissolved with the aid of heat in toluene, and the solution allowed to evaporate spontaneously, when a residue was obtained consisting of brown flat needles of iodoanil mixed with white, amorphous tetraiodohydroquinone. Again a finely powdered crystal of the quinhydrone was treated with warm benzene, to which a little alcohol had been added. On evaporating the yellow solution the white tetraiodohydroquinone could be seen floating on the surface of the liquid, and the residue, as before, contained this white substance mixed with brown crystals of iodoanil. Iodoanil treated in exactly the same way showed only these brown crystals with no white admixture. A small amount of the quinhydrone was dissolved in glacial acetic acid, when, on adding sodium hydroxide cautiously, a white precipitate was obtained, which dissolved in the excess of the alkali, and was thrown down again by dilute sulfuric acid.

When a little of the quinhydrone was treated with twice normal sodium hydroxide the crystals were at once disintegrated, losing their crystalline form and yielding a brown powder, which we suppose to be iodoanil, and a yellow solution. This was poured off at once and acidified with dilute sulfuric acid, when a white precipitate was thrown down that redissolved in sodium hydroxide and is therefore probably tetraiodohydroquinone. A parallel experiment with iodoanil showed that it did not act at all with sodium hydroxide under the same conditions.

Determination of the Relative Solubilities of Iodoanil and Octoiodoquinhydrone.—A concentrated solution of iodoanil was made by dissoving it in benzene to which a few drops of water had been added. After the solution had stood at ordinary temperatures for a day with frequent shaking to guard against supersaturation, it was saturated with sulfurous dioxide and the flask, tightly corked, was placed in a bath at the constant temperature of 17°. When the solution had reached this temperature, 50 cc. were drawn out with a pipette, evaporated to dryness in a weighed watch glass, and weighed. The securely corked flask was weighed and replaced in the constant temperature bath. After standing for two weeks black crystals of the quinhydrone were deposited, and, as the weight of the flask was found to be unaltered, this crystallization was due to the formation of a less soluble compound, and not to evaporation of the solvent. A second portion of 50 cc. was now removed and the residue from it weighed, and the same treatment repeated at the end of two months. The results were as follows:

I. Weight of iodoanil in 50 cc. of benzene 0.5060 g. II. Weight of solid in 50 cc. benzene after standing two weeks with H_2SO_3, 0.4462 g.; weight of flask after I, 380.62 g.; weight of flask just before II, 380.52 g. III. Weight of solid in 50 cc. benzene after standing for two months with H_2SO_3, 0.3698 g.; weight of flask after II, and just before III, 335.2 g.

50 cc. of the solution therefore contained 0.1362 gram less solid after the formation of the quinhydrone than it contained before, showing that the quinhydrone is less soluble than the iodoanil.

Comparison of the Behavior of Iodoanil with that of Chloroanil and of Bromoanil.—One gram of each of the three substances was dissolved in

80 cc. of benzene containing 0.5 cc. of water. Each solution was saturated with sulfurous dioxide and allowed to stand at ordinary temperatures in loosely corked flasks (since these experiments were tried before we had found that the quinhydrone crystals were deposited without any evaporation of the solvent). After four weeks the flask containing the iodoanil showed crystals, some of which were black like the quinhydrone, others brown like iodoanil, but, as the black crystals were no larger than the others, the darker color could not be due to greater thickness. This black color, which we have never observed with iodoanil alone, justifies us in inferring that the quinhydrone had been formed, and we were confirmed in this belief by the peculiarities in habit of the two sorts of crystals, for, while the black were usually terminated at both ends by two planes at an obtuse angle, the brown showed only one such termination, the other, if well developed, consisting of a single plane at right angles to the sides. From the solution of chloroanil there had been deposited large clumps of white prisms evidently tetrachlorohydroquinone mixed with a small amount of yellow unchanged chloroanil, while only a yellow deposit of bromoanil was obtained from the experiment with this compound. Neither with chloroanil nor the bromoanil was there any indication of a substance with a darker color than yellow.

Action of Iodoanil on Tetraiodohydroquinone.—To determine whether the formation of the quinhydrone required that the hydroquinone should be in the nascent state, a mixture of iodoanil and tetraiodohydroquinone, in the proportion of two molecules of the former to one of the latter, was dissolved in warm benzene. Upon cooling brown crystals of iodoanil separated and the liquid was then allowed to stand in a loosely corked flask for several weeks, when the crystals deposited were found to consist of long, slender, brown prisms and broader, black, prismatic plates, from which we infer that octoiodoquinhydrone had been formed in this case also, although in smaller quantity than in the experiment, in which the iodoanil was reduced by sulfurous acid.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE SPLITTING OF BENZHYDROLS BY THE ACTION OF BROMINE.[1]

BY GUSTAVUS J. ESSELEN, JR. AND LATHAM CLARKE.

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In the course of a research on certain substituted benzophenones and benzhydrols, the authors observed that when bromine was allowed to act on 4-aminobenzhydrol, in chloroform solution, a splitting took place, by which benzaldehyde was set free.[1] The amount of the last was small, and the principal reaction product was probably an anhydride of high molecular weight, such as that obtained by Kippenberg,[2] from 4-aminobenzhydrol by the action of hydrobromic acid. To a certain extent, however, the following reaction seemed to take place, although we were not able to isolate any bromoaniline,

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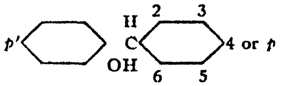
[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, Cambridge, Mass., U. S. A., for the degree of Doctor of Philosophy by Gustavus J. Esselen, Jr.

$$C_6H_5.CH(OH).C_6H_4NH_2 + Br_2 = C_6H_5CHO + BrC_6H_4NH_2 + HBr.$$

As such a reaction is entirely new, we decided to investigate it further and so prepared 3,5-dibromo-4-aminobenzhydrol, which we considered would not undergo the Kippenberg anydride reaction. When this hydrol, in chloroform solution, was treated with two atoms of bromine, the products were found to be benzaldehyde, 2,4,6-tribromoaniline and hydrobromic acid, no other compounds being formed in amounts sufficient to be detected.

That the reaction is a general one is shown by the following table, giving the compounds which have been investigated, and the products they yielded when treated with bromine in chloroform solution. Hydrobromic acid was formed in every case together with the other products indicated.

Substituents in the benzhydrol. 	Products.
1. *p*-Amino	Benzaldehyde, *p*-bromoaniline(?) anhydride
2. 3,5-Dibromo-4-amino	Benzaldehyde, 2,4,6-tribromoaniline
3. 3-Methyl-4-amino	Benzaldehyde, 3,5-dibromo-2-toluidine
4. *p*'-Nitro-*p*-monomethylamino	*p*-Nitrobenzaldehyde, *o*,*p*-dibromomonomethylaniline
5. *p*-Dimethylamino	Benzaldehyde, *p*-bromodimethylaniline
6. 3-Bromo-4-dimethylamino	Benzaldehyde, *o*,*p*-dibromodimethylaniline
7. *p*'-Nitro-*p*-dimethylamino	*p*-Nitrobenzaldehyde, *p*-bromodimethylaniline
8. *p*,*p*'-Tetramethyldiamino	*p*-Dimethylaminobenzaldehyde, *p*-bromodimethylaniline
9. *p*'-Nitro-*p*-diethylamino	*p*-Nitrobenzaldehyde, *p*-bromodimethylaniline
10. 2-Amino-5-methyl	Benzaldehyde, 3,5-dibromo-4-toluidine
11. *m*-Amino	No splitting
12. Unsubstituted[3]	No splitting

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[1] THIS JOURNAL, 33, 1135 (July, 1911).

[2] *Ber.*, 30, 1135.

[3] Linnemann [*Ann*, 133, 11 (1865)] got no splitting with bromine sealed at 200°.

In Nos. 3, 4, and 10 in the above table, one molecular proportion of bromine split only half of the hydrol present, which is explained by the fact that in each case a dibromo compound was formed.

The usual solvent was dry chloroform, free from alcohol, but alcohol-free ether and absolute alcohol serve equally well. Ether has the advantage that the aldehyde product of the splitting remains in solution, while the hydrobromide of the amino part is precipitated, thus making the separation of the products, as a rule, easy.

In brief, it has been shown that benzhydrols, with an amino or alkylated amino group in the ortho or para position to the hydrol group, are split by the action of bromine into benzaldehyde or benzaldehyde derivatives, and a halogenated aniline derivative. Chlorine and iodine act similarly to bromine with such modifications, as the differences in nature of these three elements would lead one to expect, but neither gives so good results as bromine. Benzhydrol and *m*-aminobenzhydrol do not split under the influence of bromine. Finally the reaction does not depend on the solvent in which it is carried on.

This reaction has a very practical value for organic chemistry in determining the constitution of compounds belonging to certain classes, not only the benzhydrols or benzophenones containing an amino group in the ortho or para position, or benzhydrols in which such a group could be introduced, but also the derivatives of diphenylmethane, inasmuch as these, on oxidation with chromic acid, give the corresponding benzophenone compounds which, in turn, could be reduced to the benzhydrols with sodium or aluminum amalgam, and then split with bromine.

In looking through the literature for similar examples of splitting, only one was found in any way resembling the one under consideration. Weil[1] noticed that boiling with dilute mineral acid for several days breaks up *p,p'*-tetramethyldiaminobenzhydrol into dimethylaniline and *p*-dimethylaminobenzaldehyde, which latter condenses at once in the acid solution with unchanged hydrol or with dimethylaniline to form leukocrystal violet, but when this splitting with acid is compared with the bromine splitting, several marked differences are apparent. The most striking is, that in the case of bromine the action takes place almost instantaneously even at 0°, whereas with the acid it takes several days at a temperature of about 100°. Another difference is that dimethylaniline is produced with the acid, where *p*-bromodimethylaniline is obtained in the bromine splitting. Finally some compounds, which are synthesized by heating *p*-nitrobenzaldehyde with an alkylated aniline at 100° in concentrated hydrochloric acid solution for forty hours, for example *p*-nitro-*p'*-dimethylaminobenzhydrol and *p*-nitro-*p'*-diethylaminobenzhydrol, break down at once when treated with bromine in chloroform. In these cases there can be no doubt that the splitting is not due to acid or it would not be possible to synthesize the compounds in the manner in which they are prepared. Since the other examples of the splitting are analogous to these two, this evidence may be included with the rest to show that in no case is the splitting with which this work is concerned due to hydrobromic or other mineral acid, but is caused entirely by the action of the bromine.

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[1] *Ber.*, 27, 3316 (1894).

The Mechanism of the Reaction.

Concerning the mechanism of the reaction whereby bromine splits ortho and para-aminobenzhydrols, Hantzsch and Graf[1] have shown that bromine, when allowed to act on an aromatic amine, first forms an unstable addition compound in which one molecule of bromine is directly added to nitrogen, and that this addition compound then rearranges to form the hydrobromide of a substitution product, from which the hydrobromic acid may or may not be split off according to the conditions.

If now our reaction proceeds in accordance with the work of Hantzsch and Graf, the primary product should be a compound of the general formula:

$$C_6H_5.CH(OH).C_6H_4NR_2Br.Br,$$

where R may be either hydrogen or an alkyl group. When the splitting was carried out at —80°, it was found possible to isolate intermediate compounds, which exhibited all the properties that would be expected from amine dibromides, some of which could be explained on no other basis except the assumption that they were amine dibromides. It may be objected that the splitting reaction might take place very quickly even at - 80°, and that the supposed intermediate compounds were really perbromides of the bromoamine formed by the splitting. In answer to this, it is sufficient to consider the case of *p*-dimethylaminobenzhydrol and to point out that the perbromides of *p*-bromodimethylaniline are solids,[2] are comparatively stable at room temperature and form at 0°, whereas our compound in this case was an oil and did not form even at —20°. Accordingly it is clear that the substances in question must be considered as amine dibromides even though their instability at ordinary temperatures prevented an analysis to determine their exact composition.

The next question is obviously as to how the dibromide of an aminobenzhydrol can fit into a scheme which explains the splitting of aminobenzhydrols. It will be remembered that Hantzsch and Graf[3] were unable to isolate the dibromide of dimethylaniline, because of the great tendency for one atom of bromine to change places with the parahydrogen atom of the benzene ring, thereby forming the hydrobromide of *p*-bromodimethylaniline. This rearrangement was found to take place even at —40°. Since bromine exhibits so great a tendency to shift to the para position in the ring, it would not seem surprising if the second stage in the action of bromine on aminobenzhydrol consisted in an interchange of position between one of the added atoms of bromine and the group in the para position, *viz.*, $C_6H_5CH(OH)$. The compound thus formed would be represented by the formula: $BrC_6H_4N(R_2)(Br)—CH(OH)C_6H_5$.

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[1] *Ann.*, 346, 188 (1906).

[2] *Ibid.*, 346, 195 (1906).

[3] *Loc. cit.*

Objection may be raised that the analogy is not complete; that the large group $C_6H_5CH(OH)—$ could not be expected to shift with any such readiness as an atom of hydrogen, as in the case of dimethylaniline. The answer to this is, that, in order to be dislodged by the bromine, the group in the para position need only be united to the benzene nucleus by a force which is no stronger than that which binds an atom of hydrogen in a similar position. If such is the case, the work of Hantzsch and Graf already referred to shows that it will be replaced by the bromine. Chattaway[1] has further shown that the compound, $C_6H_5N(COC_6H_5)_2$, when heated, rearranges to a compound with the formula: $C_6H_5COC_6H_4NH—COC_6H_5$. In this case the group which rearranges is $C_6H_5CO—$, quite similar to the one with which we are dealing. If this rearranges in the molten solid, the rearrangement supposed for the bromine reaction in this paper ought to go much more readily when once started, since it is carried on in solution.

It may be well to consider if there is any further evidence, other than analogy, which indicates the occurrence of a rearrangement like that just outlined. The first thing that suggests itself is the fact that when the amine dibromides of the aminobenzhydrols were put on a watch glass or porous plate at ordinary temperatures, they were agitated by some internal disturbance which may well have been due to a readjustment or rearrangement of the forces within the molecule. A strong confirmation of the theory given above is that the splitting occurs with those benzhydrols where the amino or alkylated amino group is in the para or the ortho position, but does not occur when the amino group is in the meta position. Now, it is well known that halogen, rearranging from nitrogen, tends to go into the para position if possible, and if not, then to the ortho position, but never to the meta position.

Granting, then, that such a rearrangement takes place, it requires only that a molecule of hydrobromic acid be split off, to give the products actually obtained by experiment. This molecule of hydrobromic acid may, or may not, combine with the amine according to the conditions and the nature of the amine. The mechanism of the reaction would be then as follows:

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[1] *J. Chem. Soc.*, 85, 394 (1904).

$$C_6H_5CH(OH)C_6H_4NR_2 + 2Br \longrightarrow C_6H_5CH(OH).C_6H_4NR_2BrBr \longrightarrow$$
$$C_6H_4CH(OH).N(R_2)Br.C_6H_4Br \longrightarrow C_6H_5CHO + N(R_2)C_6H_4BrHBr.$$

Experimental Part.

The preparation, properties and action of bromine on *p*-aminobenzhydrol and 3,5-dibromo-4-aminobenzhydrol have been described in an earlier paper.[1]

3-Methyl-4-aminobenzhydrol.—The preparation of 3-methyl-4-aminobenzhydrol was effected by reducing 3-methyl-4-aminobenzophenone with sodium amalgam in alcoholic solution. The 3-methyl-4-aminobenzophenone was made according to the method of Chattaway[2] and Lewis by heating *o*-toluidine with benzoyl chloride in the presence of anhydrous zinc chloride and saponifying the resulting benzoyl derivative of 3-methyl-4-aminobenzophenone. In carrying out the reduction, one part of 3-methyl-4-aminobenzophenone was dissolved in twelve parts of alcohol and to the solution were added fifteen parts of three per cent. sodium amalgam. After standing at room temperature for several hours, the mixture was heated on a steam bath with a reflux condenser for six hours, five parts of water being added to the mixture after two and a half hours. At the end of six hours the solution was filtered hot and evaporated on a steam bath until crystallization began. It was then cooled and the crystals which formed were filtered off and dried. They were crystallized from a mixture of one part of alcohol with three parts of water and a drop or two of twice normal sodium hydroxide solution. Hot benzene, hot naphtha or hot carbon tetrachloride can also be used, but none of these work so well as the dilute alcohol just referred to.

Properties.—3-Methyl-4-aminobenzhydrol crystallizes in white needles which melt at 110°. It is soluble in methyl and ethyl alcohols, ether, hot benzene, hot naphtha, chloroform, acetone, and hot carbon tetrachloride. It is insoluble in water. Concentrated nitric acid dissolves it, forming a solution which is yellow at ordinary temperature but turns red on boiling. Concentrated hydrochloric acid converts it into an amorphous body which is not soluble even in boiling sulfuric acid. It dissolves slowly in cold, concentrated sulfuric acid to form a deep red solution which darkens on heating. Cold, glacial acetic acid forms a solution with a pale red tint. On boiling, this color changes to green and on subsequent cooling a greenish yellow solid is produced which does not melt, but chars at about 210°. These facts seem to point to the formation of an anhydride, analogous to the one formed in the case of *p*-aminobenzhydrol under similar conditions. A further indication of this is the fact that, if 3-methyl-4-aminobenzhydrol is dissolved in hot water and the resulting solution boiled so that the acid fumes of the laboratory have access to it, a white, amorphous precipitate begins to form after a few minutes. This is the reason why the liquid from which the body is crystallized is always kept slightly alkaline.

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[1] THIS JOURNAL, 33, 1138 (1911).

[2] *J. Chem. Soc.*, 85, 591 (1904).

Calculated for $C_{14}H_{15}ON$: N, 6.57%; found, 6.59%.

Action of Bromine on 3-Methyl-4-aminobenzhydrol.—3.5 g. of 3-methyl-4-aminobenzhydrol were dissolved in 70 cc. of chloroform (which had been washed three times with water and thoroughly dried) and treated with 2.63 g. (corresponding to two molecules) of bromine. The action generated a considerable amount of heat. After standing a minute or two, a white precipitate appeared in the solution and was filtered off, but it was so very small in amount that it could not be identified. The chloroform filtrate was evaporated in a rapid current of air, leaving an oily residue with a benzaldehyde odor, which was shaken with 1 : 4-hydrochloric acid. The resulting solution was almost neutralized with sodium hydroxide, extracted with ether and evaporated, leaving an oil, which was proved to be benzaldehyde by converting it to the phenylhydrazone. This, after four crystallizations, formed white, shining needles, which turned pink when exposed to the light, and melted at 153–154°, thus corresponding to the phenylhydrazone of benzaldehyde.

The residue from the extraction with hydrochloric acid was covered with very dilute acid and distilled with steam. A pale, yellow oil came over which solidified to a pale green, crystalline solid. It melted at 46.5° and sublimed to form white needles which contained halogen and melted at 46.5–47°. After two crystallizations from 25% alcohol and one from 35% alcohol, it melted at exactly the same temperature. It appeared that we were dealing with 3,5-dibromo-2-toluidine, which melts at 45–46°, according to Neville and Winther,[1] and at 50° according to Wroblevsky,[2] the latter figure being given also by Möhlau and Oehmichen.[3] After the elaborate purification process which it had undergone there was not enough of this dibromotoluidine left to analyze. Accordingly some 3,5-dibromo-2-toluidine was synthesized by treating *o*-toluidine dissolved in chloroform with bromine. The conditions of the synthesis were thus almost identical with those under which the compound was formed, when 3-methyl-4-aminobenzhydrol was split by the action of bromine. One sample of the resulting hydrobromide of 3,5-dibromo-2-toluidine was converted to the free base and purified by crystallizing from hot 50% alcohol. It then had the constant melting point 47°.

Calc for $C_7H_7NBr_2$: Br, 60.35; found, 60 69.

Action of Bromine on p-Nitro-p′-methylaminobenzhydrol.—The method used in preparing *p*-nitro-*p*′-methylaminobenzhydrol was that of Albrecht,[1] which consists essentially in heating *p*-nitrobenzaldehyde with monomethyl aniline in the presence of an excess of concentrated hydrochloric acid for forty hours on a steam bath. On dilution with water the unchanged nitrobenzaldehyde separated out and was filtered off. The filtrate was made alkaline with sodium hydroxide solution, the resulting precipitate distilled with steam to free it from unchanged methylaniline, and the residue was crystallized from 25% alcohol, giving fine, yellow needles, which melted at 113°, as against 108°, given by Albrecht as the melting point of the same compound.

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[1] *Ber.*, 13, 966 (1880).

[2] *Ann.*, 168, 187 (1873).

[3] *J. prakt. Chem.*, [2] 24, 478 (1881).

In studying the action of bromine on *p* nitro-*p'*-methylaminobenzhydrol, 2.5 g. of the substance were dissolved in 60 cc. of chloroform and to the solution 1 5 g. (corresponding to one molecule) of bromine were added. A small amount of a black oil was thrown out of solution at once. It was not volatile with steam and its identity could not be established. The solution was poured off from the black oil and the chloroform evaporated, leaving a green, partly crystalline substance. This was washed three times with ether and the insoluble residue distilled with steam, yielding a very small amount of yellow oil and a yellow solution. The oil was removed and combined with more of the same obtained from the ether washings, as will be described in a moment. On cooling the yellow solution, crystals separated out, which, after four crystallizations from water, formed long, slender, white needles and melted at 105°. They were thus identified as *p*-nitrobenzaldehyde, the melting point of which is given by Otto Fischer as 106°.[2] Our compound also had the characteristic aldehyde odor which he mentions. The ether extract of the residue left from the evaporation of the chloroform was evaporated and the resulting oil distilled with steam. The yellow oil which came over solidified on cooling, and when boiled with water, a small part of it dissolved, the solution depositing, when cool, a very small amount of pale yellow needles which proved to be *p*-nitrobenzaldehyde. The part insoluble in water was crystallized from dilute alcohol, forming white shining plates with a yellowish tinge. They were recognized as *o*-*p*-dibromomonomethyl aniline, melted at 47°, and had the other properties of that compound as given by Fries.[3]

Action of Bromine on p-Dimethylaminobenzhydrol.—The *p*-dimethylaminobenzhydrol used in this work was made by reducing *p*-dimethylaminobenzophenone with sodium amalgam according to the directions of Albrecht.[4] The most convenient method for preparing *p*-dimethylaminobenzophenone consisted in heating benzanilide with dimethylaniline in the presence of phosphorus oxychloride and pouring the product into water;[1] although the first *p*-dimethylaminobenzophenone used in this work was made according to the method of Döbner,[2] *viz.*, heating *p*-aminobenzophenone in a sealed tube with methyl alcohol and methyl iodide.

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[1] *Ber.*, **21**, 3292 (1888).

[2] *Ibid.*, **14**, 2525 (1881).

[3] *Ibid.*, **37**, 2346 (1904).

[4] *Ibid.*, **21**, 3293 (1888).

Five grams of *p*-dimethylaminobenzhydrol were dissolved in 80 cc. of chloroform and two molecular proportions of bromine added. Dry hydrogen chloride was then passed into the solution in excess to form the hydrochloride of any amine present. When the chloroform was evaporated, a green liquid was left, from which a pale yellow oil was extracted by ether. This yellow oil had the characteristic odor of benzaldehyde and boiled at 179°, which is the value given by Kopp as the boiling point of benzaldehyde.[3] In another experiment the benzaldehyde was identified by forming the characteristic phenylhydrazone which melted at 156°. The part of the green liquid insoluble in ether was dissolved in absolute alcohol and made alkaline by the addition of 4 5 g. of sodium hydroxide. The residue left after the evaporation of the alcohol was distilled with steam, giving white, waxy plates. Since these smelled noticeably of benzaldehyde, they were spread out in a thin layer and exposed to the air for three days, during which time the benzaldehyde was oxidized to benzoic acid. To get rid of this acid, the solid was washed, first with 6% sodium hydroxide solution and then with pure water. After being subjected to steam distillation, the substance melted at 53° and was analyzed for bromine.

Calc. for $C_8H_{10}NBr$: Br, 39 99; found, 40 37.

Thus the compound was parabromodimethylaniline.

Action of Bromine on p-Dimethylaminobenzhydrol at -80°.—In studying the action of bromine on *p*-dimethylaminobenzhydrol at low temperatures two kinds of experiments were performed. In the first an amount of bromine proportional to two atoms was used and in the second an amount proportional to one atom. For example, in an experiment of the first kind 2 g. of *p*-dimethylaminobenzhydrol were dissolved in 5 cc. of chloroform in a small Erlenmeyer flask, and cooled in a mixture of ether and carbon dioxide snow. A solution of 1.42 g. of bromine in 5 cc. of chloroform was prepared and similarly cooled. When this was added to the other solution a dark red oil separated out as soon as the one solution came in contact with the other. A little of the red oil taken out on a platinum spatula and put on a porous plate at room temperature turned to a very pale red color and was apparently agitated by some reaction for a few seconds. After this the odor of benzaldehyde was noticeable. In some cases a few bubbles of gas appeared during the agitation on the porous plate, probably due to the vaporization by the heat of reaction, of the small film of chloroform which still clung to the oil. The chloroform was now poured off from the main part of the oil in the original flask and acetone added in its place. The oil dissolved slowly, and at the end of an hour or so, the odor of benzaldehyde was unmistakable, as was also the characteristic effect on the eyes and nose of bromoacetone.

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[1] German patent, No. 41,751; Friedländer, I, 44.

[2] *Ann.*, 210, 270 (1881).

[3] *Ibid.*, 94, 314 (1855).

In an experiment of the second class, solutions of 2 g. of *p*-dimethylaminobenzhydrol and 0.71 g. of bromine, each in 5 cc. of chloroform, were prepared, cooled and mixed as before. A little of the red oil which formed immediately was taken out on a platinum spatula and quickly put into an aqueous solution of starch and potassium iodide, cooled to its freezing point. The characteristic blue color produced by free iodine was developed at once and was further identified by the fact that arsenious acid caused it to disappear. In order to make absolutlely sure that the test was due to an amine dibromide and not to unused bromine, some of the red oil was prepared at -80°, exactly as it was in the first experiment described above. The mother liquor was then poured off and the oil was washed three times with chloroform which had been shaken out with water, carefully dried, and cooled to its freezing point. The third washing was shaken with an aqueous solution of starch and potassic iodide, but only an exceedingly faint bluish tinge was developed, showing that all the free bromine, if any had not reacted, had been removed. A little of the red oil was then put into a similar starch-potassic iodide solution and a very deep blue color was developed which clearly showed that the oil was an amine dibromide.

3-Bromo-4-dimethylaminobenzophenone.- The simplest procedure for preparing 3-bromo-4-dimethylaminobenzophenone was found to be the following: 12 g. of *p*-dimethylaminobenzophenone were dissolved in 82 cc. of ordinary chloroform and to the solution was added 8.5 g. (corresponding to one molecule) of bromine, the color of the bromine disappearing as soon as it dissolved in the chloroform. After standing for a short time the chloroform was evaporated on a steam bath, leaving a colorless oil which was crystallized from 80% alcohol. Yield, 10 grams.

3-Bromo-4-dimethylaminobenzophenone was first obtained in an experiment, the object of which was to prepare 3-5-dibromo-4-dimethyl aminobenzophenone. It was found that but one atom of bromine could be introduced into 4-dimethylaminobenzophenone, an excess of bromine giving only a perbromide from which acetone, alcohol and potash form the above monobromo derivative. Nor did we succeed in producing the 3-5-dibromo-4-dimethylaminobenzophenone by methylation of 3-5-dibromo-4-aminobenzophenone.

Properties.—3-Bromo-4-dimethylaminobenzophenone can easily be crystallized from hot alcohol or hot naphtha. It forms colorless, transparent rhombic plates when allowed to crystallize by the spontaneous evaporation of a solvent. When crystallized from hot alcohol, it forms white, shining crystals, and melts when pure at 80°. It is soluble in ether, benzene, chloroform, carbon tetrachloride, glacial acetic acid, acetone, hot alcohol, and hot naphtha, but insoluble in water.

3-Bromo-4-dimethylaminobenzhydrol.—The first reducing agent tried in the reduction of 3-bromo-4-dimethylaminobenzophenone to the corresponding hydrol was zinc and acetic acid. This, however, did not apparently accomplish the desired result. Aluminum amalgam was next tried in the following manner. A solution of five grams of 3-bromo-4-dimethylaminobenzophenone in 150 cc. of alcohol was prepared and treated with aluminum amalgam from 25 grams of aluminum punchings. The mixture stood at room temperature for four hours and there was then added to it 8 cc. of water and aluminum amalgam from 13 g. of aluminum punchings. After standing for about eighteen hours longer, the solution was filtered from aluminum hydroxide, aluminum, and mercury, and the precipitate was washed with warm alcohol. (If the mixture was heated to the temperature of the steam bath for any length of time during the reduction, a dark green color was developed which did not appear if the reduction was carried out at the ordinary temperature of the room. In one such instance where the green color was developed quite strongly, a faint odor of benzaldehyde seemed to be perceptible after the evaporation of the alcohol.) The alcoholic filtrate was evaporated on a steam bath, leaving a yellow oil which contained halogen and gave benzaldehyde when treated with bromine in chloroform. All attempts to crystallize it, however, were in vain. A sample was prepared and dissolved in ether. The ethereal solution was dried, by standing over fused calcium chloride several days, and was then filtered and the ether evaporated carefully on a steam bath. After the residual oil had been dried *in vacuo* over stick potassium hydroxide for forty-eight hours, it was analyzed with the following results:

Calc. for $C_{15}H_{16}ONBr$. Br, 26.12%; found, 24.88%.

Properties.—3-Bromo-4-dimethylaminobenzhydrol is a straw colored, viscous oil which is not volatile with steam, and boils with decomposition at about 275° under a pressure of 55–60° mm. A certain amount of charring accompanies the distillation. It is miscible with ether, benzene, hot naphtha, hot alcohol, chloroform, carbon tetrachloride, acetone, and glacial acetic acid, but not miscible with water.

Action of Bromine on 3-Bromo-4-dimethylaminobenzhydrol.—2 g. of 3-bromo-4-dimethylaminobenzhydrol were dissolved in 10 cc. of washed dried chloroform and to the solution was added an amount of bromine corresponding to two atoms. A red oil was thrown out of solution at once, but dissolved when stirred up for a few seconds. After the chloroform had been evaporated in a rapid stream of air, a dark brown oil was left, from which ether extracted a yellow oil which had the odor of benzaldehyde and which gave a phenylhydrazone melting at 150° after one crystallization. The oil which did not dissolve in the ether was covered with water, rendered slightly acid with sulfuric acid, and distilled with steam. The colorless oil which came over with the water was identified as benzaldehyde by forming its phenylhydrazone. When there was no longer any suspended material in the distilling flask, the receivers were changed, the acid liquid in the boiling flask was made barely alkaline and the steam distillation continued. A white oil now came over which had the odor of *o-p*-dibromodimethylaniline. There can be no doubt but that the compound was really *o-p*-dibromodimethylaniline, but through an accident the material was lost, and further study was not possible.

Action of Bromine on 3-Bromo-4-dimethylaminobenzhydrol at 80°.—The action of bromine on 3-bromo-4-dimethylaminobenzhydrol at −80° was tried in exactly the same way as the last experiment described under the heading "Action of Bromine on *p*-Dimethylaminobenzhydrol at −80°." The only difference was that in this case a red solid was produced when the bromine was added where formerly a red oil was formed. The solid behaved exactly as did the oil, showing those properties which could be expected if the bromine had added to the nitrogen, but it was so unstable at ordinary temperatures that an analysis was quite out of the question.

Action of Bromine on p-Nitro-p′-dimethylaminobenzhydrol.—Four grams of *p*-nitro-*p′*-dimethylaminobenzhydrol were dissolved in 30 cc. of chloroform and 2.35 g. (corresponding to one molecule) of bromine were added and allowed to stand for a little more than an hour. The crystalline residue left after evaporating the chloroform was washed with ether several times, and the ether distilled, leaving a yellow solid with an aromatic odor which, when crystallized from water six times, formed long, pale yellow needles, melting at 105°, and corresponding entirely with the *p*-nitrobenzaldehyde described by Otto Fischer.[1] The part of the reaction product insoluble in ether was dissolved in an alcoholic solution of sodium hydroxide, the alcohol was evaporated, the residue extracted with ether, and dry hydrogen chloride was then passed into the ethereal extract. The oil which formed was separated from the solution, covered with dilute alkali, and distilled with steam. The white solid which crystallized from the distillate in waxy plates contained halogen and was purified by three crystallizations from alcohol, when it had the melting point 54°. This combined with its unmistakable odor and its other properties, identified it as *p*-bromodimethylaniline. A portion of the reaction mixture which was evaporated at once also showed the presence of *p*-bromodimethylaniline, showing that our splitting took place very quickly.

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[1] *Ber.*, 14, 2525 (1881).

The *p*-nitro-*p'*-dimethylaminobenzhydrol used in the work which has just been described was prepared by condensing dimethylaniline with *p*-nitrobenzaldehyde in the presence of an excess of hydrochloric acid.[1] The product was purified by crystallizing it from alcohol after the excess of dimethylaniline had been driven off by a rapid current of steam.

Action of Bromine on p-p'-Tetramethyldiaminobenzhydrol.—In studying the action of bromine on *p*-*p'*-tetramethyldiaminobenzhydrol, it was found that the temperature played quite an important part in determining how far the reaction went. If the chloroform, after the addition of the bromine to the chloroform solution of the benzhydrol, was evaporated on the steam bath, *p*-dimethylaminobenzaldehyde was identified without difficulty as one of the products of the reaction, but the other was a blue solid which behaved like a dye analogous to crystal violet, and no *p*-bromodimethylaniline could be found, although many varied attempts were made to detect it. However, this result was obtained as follows 7.5 g. of *p*-*p'*-tetramethyldiaminobenzhydrol (prepared by reducing Michler's ketone with sodium amalgam[2]) were dissolved in 50 cc. of chloroform and treated with 4.4 g. of bromine, which was proportional to one molecule. Heat was generated by the reaction and the solution turned dark blue in color. On evaporating the chloroform in a rapid current of air, at room temperature instead of on the steam bath, a blue crystalline mass was left which had an odor like *p*-bromodimethylaniline. It was distilled with steam and the distillate collected in three fractions of about 300 cc. each. In the first fraction, on cooling, white waxy plates formed, which, after three crystallizations from alcohol, melted at 54° and had the characteristic odor of *p*-bromodimethylaniline.

Calc for $C_8H_{10}NBr$; Br, 39 99, found, 40 33%

The second fraction of the distillate, after a small amount of *p*-bromodimethylaniline had been filtered out, was treated with a few drops of alcohol and then with a little phenylhydrazine, which produced a white precipitate. When crystallized four times from water, this precipitate formed pale yellow, shining needles, which melted at 146 5° and corresponded in their properties with the phenylhydrazone of *p*-dimethylaminobenzaldehyde, which melts according to Knofler and Boessneck[3] at 148°. The presence of *p*-dimethylaminobenzaldehyde in the third fraction of the distillate was shown by adding, after slight acidification with hydrochloric acid, a few drops of benzidine in water which produced a yellow color and at the end of about three-quarters of an hour the brick-red precipitate characteristic of *p*-dimethylaminobenzaldehyde according to Weil.[4]

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[1] Albrecht, *Ber.*, 21, 3292 (1888); German patent, No. 45,806.

[2] Nathanson and Müller, *Ber.*, 22, 1879 1889).

[3] *Ber*, 20, 3195 (1887)

[4] *Ibid*, 27, 3317 (1894).

Action of Bromine on p-Nitro-p'-diethylaminobenzhydrol.—In preparing the *p*-nitro-*p'*-diethylaminobenzhydrol which was used in this work, the method of Albrecht[1] was used, consisting in condensing *p*-nitrobenzaldehyde with diethylaniline in the presence of an excess of hydrochloric acid. 1.4 g. of *p*-nitro-*p'*-diethylaminobenzhydrol were dissolved in 10 cc. of dry chloroform and an amount of bromine corresponding to one molecule was added. The chloroform was evaporated in a rapid current of air, leaving a yellowish crystalline residue. Ether extracted from this a solid, which, after five crystallizations from water, melted at 105° and was identical in its other properties with the *p*-nitrobenzaldehyde described by O. Fischer. The residue, left after washing with ether, was subjected to steam distillation, first from a dilute sulfuric acid solution to get rid of the remaining *p*-nitrobenzaldehyde, and later from a slightly alkaline solution, yielding a sweet-smelling, colorless oil, which crystallized on cooling to form cream-colored plates containing halogen. When crystallized once from alcohol it formed white needles which melted at 33° and corresponded in every way with the *p*-bromodiethylanilin described by Claus and Howitz.[2]

2-Amino-5-methylbenzhydrol.—3-Methyl-4-aminobenzophenone was made by heating *p*-toluidine with benzoyl chloride, in the presence of anhydrous zinc chloride, for a number of hours.[3] After a saponification with alcoholic hydrochloric acid and removal of ethyl benzoate and tarry matters, the 3-methyl-4-aminobenzophenone was obtained by means of a long-continued steam distillation. In reducing this to the benzhydrol one part was dissolved in twelve parts of alcohol and fifteen parts of 3% sodium amalgam were added. After standing for two or three hours at room temperature, the mixture was boiled under a return condenser for six hours or until all the amalgam was exhausted, four parts of water being added at the end of three hours of heating. The solution was filtered hot and evaporated on a steam bath to about half of its original volume, when an oil separated out, and, on cooling, this solidified in white, radiating, circular clumps, which were crystallized from a mixture of one part of alcohol to four of water, the mixture being made alkaline with a few drops of twice normal sodium hydroxide. Two or three crystallizations were sufficient for purification. This compound was 2-amino-5-methylbenzhydrol.

Calc for $C_{14}H_{15}NO$: N 6.57; found 6.62, 6.65%.

Properties.—When crystallized from slightly alkaline 20% alcohol, 2-amino-5-methylbenzhydrol forms white, feathery crystals or small, shining transparent rhombohedra. When dissolved in alcohol and allowed to crystallize undisturbed by the spontaneous evaporation of the solvent, it forms large, well-formed transparent rhombohedra. It melts, when pure, at 107°. It is soluble in alcohol, ether, benzene, chloroform, acetone, glacial acetic acid, hot naphtha, carbon tetrachloride (somewhat soluble in the cold also) and hot water. It is only very slightly soluble in cold water or cold naphtha. Concentrated nitric acid dissolves 2-amino-5-methylbenzhydrol in the cold, forming a pale yellow solution which turns a deeper shade on boiling. When treated with cold concentrated hydrochloric acid it seems to dissolve, but in a few seconds a turbidity appears which dissolves on boiling, but reappears when the solution is cooled. Concentrated sulfuric acid dissolves it to form a red solution, which chars when heated.

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[1] *Loc. cit.*

[2] *Ber.*, 17, 1327 (1884).

[3] Chattaway and Lewis, *J. Chem. Soc.*, 85, 594 (1904).

Action of Bromine on 2-Amino-5-methylbenzhydrol.—In this experiment, the object of which was to see if an amino group in the ortho position to the hydrol group behaved like one in the para position, 2 1 g. of 2-amino-5-methylbenzhydrol were dissolved in 20 cc. of chloroform. On the addition of 1.58 g. (one molecule) of bromine a noticeable amount of heat was generated. The chloroform was evaporated at once by a stream of air, leaving a yellow oil which had the odor of benzaldehyde. It was washed five times with 20 cc. portions of 1 : 1 hydrochloric acid, leaving an insoluble residue which was not volatile with steam, being probably, for the most part, unchanged 2-amino-5-methylbenzhydrol. The hydrochloric acid washings were subjected to a steam distillation, and white needles were obtained, melting at 73°, and identical in every respect with the 3,5-dibromo-4-toluidine of Wroblewsky.[1] Nothing was obtained by further distilling after addition of an alkali. The filtrate from the white needles was proven to contain benzaldehyde by the formation of its phenylhydrazone[2] melting at 155.5°.

Meta-aminobenzhydrol.—*m*-Aminobenzophenone was made as follows: The chloride of *m*-nitrobenzoic[3] acid was condensed with pure benzene by means of anhydrous aluminum chloride.[4] It was found that only about one-third the amount of aluminum chloride given in the literature was needed. The resulting *m*-nitrobenzophenone was then converted to *m*-aminobenzophenone by reduction with stannous chloride in alcoholic hydrochloric acid. To reduce *m*-aminobenzophenone to *m*-aminobenzhydrol, one part of the former was dissolved in thirty-five parts of alcohol and twelve parts of 3% sodium amalgam were added. After standing over night at the ordinary temperature of the room, the mixture was heated with reflux condenser for two and a half hours and the procedure repeated. The solution was then filtered hot and evaporated to a syrupy consistency. When diluted with water and allowed to stand in a cool place, a white solid formed, which was purified by repeated crystallization from water or from a mixture of one part of alcohol to nine parts of water.

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[1] *Ann.*, 168, 188 (1873).

[2] *Loc. cit.*

[3] *Ber.*, 12, 1943 (1870).

[4] *Ibid.*, 18, 2401 (1886).

Calc. for $C_{13}H_{13}ON$: N, 7.04; found, 6.98%.

Properties.—Meta-aminobenzhydrol is a white solid which crystallizes in radiating clusters of needles or in small, transparent rhombohedra. It is soluble in alcohol, ether, benzene, chloroform, acetone, and glacial acetic acid, but practically insoluble in cold water, cold naphtha, and cold carbon tetrachloride. It is, however, soluble in the last three solvents hot. The melting point of *m*-aminobenzhydrol is a little peculiar. The substance usually melts when pure at 78°. In some cases, after a melting point of 78° had been obtained, another crystallization gave a solid which softened a little at 64°, but did not melt until a temperature of 76–77° was reached. All the crystallizations were carried out apparently under the same conditions, and the slight variation, if any, which caused the production of solids with different melting points could not be detected. It seems possible that the variation may be due to water of crystallization. In support of this idea it may be noted that a sample of the solid which melted at 64° was allowed to stand in a desiccator over caustic potash for ten days, after which it melted at 77°.

Action of Bromine on m-Aminobenzhydrol.—Bromine in chloroform solution when added to chloroform solutions of *m* aminobenzhydrol, yielded nothing other than a yellow oil, which refused to crystallize. Experiments were carried out, in both hot and cold solvents, also using an excess of bromine, but with no better result. The reaction product certainly contained no benzaldehyde. It might well have been an anhydride formed by elimination of water from the hydroxyl and amino groups, analogous to the anhydride of Kippenberg, but this was not proved. However, the important point was established that *m*-aminobenzhydrol does not split down into benzaldehyde and bromoaniline under the influence of bromine.

Action of Bromine on Benzhydrol.—No splitting of benzhydrol was brought about by bromine, although tried under various conditions. Linneman[1] states that benzhydrol, when heated with bromine in a sealed tube for several hours at 200°, yields dibromobenzhydrol.

Action of Chlorine on p-Dimethylaminobenzhydrol.—A stream of dry chlorine gas, at the rate of 150 bubbles per minute, was passed for four minutes through a solution of 2.5 g. of *p*-dimethylaminobenzhydrol in 15 cc. of chloroform. The chlorine was generated by the action of hydrochloric acid on bleaching powder. It was freed from hydrochloric acid by passing through a tower containing water and then dried by concentrated sulphuric acid. A considerable amount of heat was generated and the solution took on a slight green tinge. At the end of the four minutes the chloroform was evaporated in a rapid stream of air, the last traces being driven off at 100°. A green oil remained which had the odor of benzaldehyde. The odor was not very strong, but still unmistakable. The oil was washed three times with boiling ether, which removed a very small amount of a yellow oil with the benzaldehyde odor. The residue, insoluble in ether, when subjected to a steam distillation, from either very dilute acid or very dilute alkali, gave a small amount of a colorless oil which had an odor not unlike *p*-bromodimethylaniline and probably was *p*-chlorodimethylaniline. A non-volatile residue was left which was apparently, for the most part, *p*-dimethylaminobenzhydrol, since it gave the characteristic splitting with bromine in chloroform solution. From this experiment, it seemed probable that a splitting had occurred, inasmuch as the odor of benzaldehyde was noticeable at so many points in the procedure, but that the chlorine had acted further to form other products which could not be readily identified. Several modifications of the above procedure were tried, and in one case the temperature of the hydrol solution was maintained at -70-80°, but no better success attended these efforts.

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[1] *Ann.*, 133, 11 (1865).

Action of Iodine on p-Dimethylaminobenzhydrol.—Iodine in chloroform solution split *p*-dimethylaminobenzhydrol into benzaldehyde and other substances which could not be identified. The reaction does not proceed at all smoothly, and although tried under widely varying conditions only benzaldehyde was isolated. The latter was recognized through its odor, and the physical properties of its phenylhydrazone.

Use of Solvents Other than Chloroform.—*p*-Dimethylaminobenzhydrol in absolute ether solution, when treated with bromine in absolute ether, was at once split into benzaldehyde and the hydrobromide of parabromodimethylaniline, the former remaining in solution, the latter being thrown down as a reddish precipitate. The benzaldehyde was identified by conversion into its phenylhydrazone. The hydrobromide of parabromodimethylaniline was decomposed by alkali, giving the free base which was identified by its physical properties. The splitting took place equally well when absolute alcohol was employed as the solvent. In this case, after distilling off the alcohol, the two products were separated, first by distilling from acid aqueous solution which gave benzaldehyde, and second from alkaline solution, which gave the parabromodimethylaniline.

We wish to express our thanks to Messrs. Kalle & Co., who very kindly furnished the meta- and paranitrobenzaldehydes used in this work. We are also much indebted to the Cyrus M. Warren Fund for aid in defraying our research expenses.

CAMBRIDGE, MASS.

ON ABIETIC ACID AND SOME OF ITS SALTS.

By Emil Oscar Ellingson.

Received December 3, 1913.

One of the first investigators who succeeded in isolating a crystalline substance from colophony was Baup.[1] To the crystalline material obtained from the colophony of the *Pinus Abies* tree he gave the name abietic acid. Since the time of Baup many experimental results have been contributed to the study of this acid, but in several instances they do not agree. For example, the melting point of the substance on record varies to such an extent that one may be inclined to question the purity of the acid studied.

Although the subject of this paper deals, in general, with the preparation of abietic acid and its salts, the chief object of the investigation was to isolate the acid in the purest obtainable condition and to compare the product with that described in the literature.

Abietic Acid.

The abietic acid prepared by the writer was obtained from commercial colophony, the method of preparation being similar to that employed by Maly.[2] His method consists mainly in extracting the rosin by means of 70% alcohol at about 50°, after which the undissolved residue is recrystallized several times from about 85% hot alcohol by adding some water to the solution to make the acid crystallize out more rapidly.

The acid described in this paper was prepared in the following manner: To 1500 grams of 70% alcohol about 800 grams of rosin are added and the mixture heated on a boiling water bath for thirty minutes. A five-liter Jena flask may be used as a container. Part of the rosin dissolves, coloring the alcohol yellow, and the remainder forms a reddish yellow liquid immiscible with the alcoholic solution. When the container is shaken vigorously the mixture assumes the appearance of a white emulsion. On standing in a cool place, the emulsion separates into two distinct liquid layers, of which the lower one solidifies after a few hours to a yellow, granular mass. The supernatant liquid is poured off from the hardened layer and the latter again extracted in a fresh quantity of 70% alcohol and otherwise treated in the same way. This procedure is repeated once more, after which the final residue is recrystallized about seven times from hot 95% alcohol without the addition of water. A few cubic centimeters of acetic acid, added to the solution when recrystallizing the first time, seemed to aid the process of crystallization. Emmerling[3] allowed the acid to crystallize from concentrated acetic acid before attempting to recrystallize it from alcohol.

If water be added to start the precipitation of the acid, the latter crystallizes fairly rapidly but the compound is not pure, the crystals occluding an appreciable quantity of other resinous materials from the solution. It was found that some of these impurities clung to the acid even when no water was added. The complete separation of the acid from this admixture of resinous substance constitutes the main difficulty in securing the pure compound.

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[1] *Ann. chim. phys.*, 31, 108 (1826).

[2] *J. prakt. Chem.*, 86, 111 (1862).

[3] *Ber.*, 12, 1442 (1879).

To obtain pure abietic acid it should be allowed to crystallize slowly from a hot solution of 95% alcohol, in which from 10% to 15% of the acid has been dissolved, repeating the process until the compound shows a definite melting point. The alcoholic solution is placed in a large crystallizing dish and about one-third or one-half of the solvent allowed to evaporate spontaneously at room temperature. The crystals are then drained free from the remaining mother liquor.

As the recrystallization proceeds, the crystals gradually become larger and more distinct and, finally, the acid appears in the shape of transparent, colorless, triangular plates. The accompanying photograph was taken of the crystals remaining in the crystallizing dish after the removal of the mother liquor. The shape of the crystals corresponds to that usually described for abietic acid The largest crystals measured one centimeter on an edge, which is somewhat more than the usual size heretofore obtained.

Ordinarily, abietic acid is said to be a crystalline compound of a light yellow color, but the crystals obtained by the writer were perfectly colorless. While this is evidence of the high purity of the compound, the crystals were, nevertheless, observed to be coated with a very thin, sticky material. To eliminate this impurity, the crystals were further recrystallized several times from 95% alcohol, but it was impossible to get rid, entirely, of the final traces of the foreign substance. Whether the contamination is due to a resinous impurity not properly removed, or to a slight decomposition of the crystalline acid to non-crystalline substances was not ascertained. It is possible that a gradual oxidation or some other chemical change takes place when the acid is in contact with alcohol and atmospheric oxygen.

The melting point was determined in the usual way, beginning with the sample obtained from the first recrystallization of the extracted residue. With each successive crystallization the melting point rose gradually from 120°, for the less pure material, to 152° for the pure acid. Since the latter invariably appeared to be melted at 152°, this temperature was taken as the melting point of the pure compound.

It should be mentioned in this connection that the rate at which the acid is heated has a marked influence on the observed melting point. If the rate of rise in temperature be about one degree per three or four minutes, the crystals begin to soften at 142°-146°, whereas if the rate be about two degrees per minute they do not melt below 152° and are sometimes not wholly melted until a temperature of 155° has been registered. However, when the rate is regulated to about one degree per minute the compound starts to melt at or near 150° and is entirely melted at 152°. By thus moderating the rate any decomposition due to prolonged heating is reduced, and any possible discrepancy existing between the thermometer reading and the actual temperature of the melting acid, due to too rapid heating, is minimized.

From these observations it seems that the acid is not characterized by a sharp melting point. According to Schwalbe,[1] abietic acid decomposes on heating above 120°, giving off carbon dioxide. That rosin and abietic acid give off vapors when melting is a well known fact. These fumes contain hydrocarbons. Such a behavior would naturally result in a somewhat variable melting point in the acid.

In the literature one finds the melting point given by different investigators varying all the way from 120° to 182°. Thus, Maly[2] found it to be 165°, Emmerling[3] 139°, Flückiger[4] from 120° to 135°, Mead and Kremers[5] from 150° to 156°, Levy[6] 182°, Loos[7] from 149° to 161°, and Frankforter[8] 130°. This wide discrepancy cannot be due to the impurity of the acid under consideration but rather to the formation of isomerides whose properties may differ greatly. The variation of about two degrees in the melting point of the acid examined by the writer is therefore very satisfactory. It is well known that resinous compounds do not, as a rule, exhibit a perfectly sharp melting point.

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[1] *Z. angew. Chem*., **18**, 1852 (1905)

[2] *J prakt. Chem*., **92**, 2 (1864).

[3] *Ber*., **12**, 1442 (1879).

[4] *J. prakt. Chem*., **101**, 239 (1867).

[5] *Proc. Am. Pharm. Assoc*., **41**, 204 (1893)

[6] *Z. angew. Chem*., **18**, 1739 (1905).

[7] *Dissert*., **1900**, published by the Chemical Publishing Co., Easton, Pa.

[8] THIS JOURNAL, **31**, 536 (1909).

In the process of melting, the colorless acid became reddish brown. The coloration is probably caused by a chemical action going on in the compound at higher temperatures. That a change has taken place is further shown by the appreciable non-crystalline, resinous residue that remains after evaporating the mother liquor taken from a recrystallization of the melted acid in alcohol.

Another proof that a chemical change occurs in the acid during melting is that the heat of combustion of the melted acid is a little lower than that of the unmelted compound. Since the heat of combustion is less for the melted than for the unmelted acid the change seems to be one of oxidation. It is, therefore, evident that this slight alteration in the composition of abietic acid, near its melting temperature, accounts for the fact that the melting point is not a sharp one.

The yield of abietic acid obtained from the colophony at hand was only about 10%. According to some experimenters yields as high as 83% have been reached. The low percentage realized by the writer refers strictly to the pure acid. Undoubtedly some of it remained in the mother liquors, mixed with the resinous substances, from which it would be difficult to isolate the acid in the pure condition by fractional crystallization. No attempts were made to recover the part which may have been lost in this way.

The formula of abietic acid is either $C_{19}H_{28}O_2$ or $C_{20}H_{30}O_2$, preferably the latter. The corresponding molecular weights are 288 and 302, respectively. Experiments on the molecular weight of the acid prepared as just described were made according to both the freezing- and boiling-point methods. The boiling was done by electrical heating. The results of these determinations are shown in Tables I and II.

The results obtained in a given solvent by the cryoscopic method are fairly concordant. There is, however, a marked disagreement in the data for the *different* solvents. The results in benzene (Table I) indicate that the acid molecules are associated in this solvent.

Abietic acid is readily soluble in most organic liquids, the solutions formed being non-electrolytes. Attempts were made to pass an electric current through 1% solutions of the acid in pyridine, acetic acid, alcohol, benzene, and phenol, at temperatures ranging from 25° to 75°. A conductance slightly above that of the pure solvent was noticed only in the pyridine solution. This solution was, therefore, investigated further to ascertain if the acid and pyridine had combined to form an abietate of pyridine in solution. About five grams of the acid were dissolved in twenty grams of pyridine and the solution carefully distilled under reduced pressure to separate the product of the interaction of the acid and the base. No such compound could be isolated in this way, for the base distilled off pure and the acid remained in the retort as a brown rosin-like mass. Solutions of the acid in aniline, dimethylaniline, and amylamine were similarly treated and with the same results. Mach[1] succeeded in preparing a crystalline, water-soluble compound, by allowing the much stronger base, tetramethyl ammonium hydroxide, to act on the acid. The product, however, decomposed rapidly on exposure to the air.

MOLECULAR WEIGHT.

TABLE I.—FREEZING POINT METHOD.

Solvent used	Grams of acid in 100 grams of solvent	Lowering of the F. P. Degrees.	Corresponding mol. wt.
Acetic acid. Mol. depression, 3880	0.9924	0.141	272
	1.1422	0.168	263
	1.6272	0.236	267
	2.2720	0.319	275
Benzene. Mol. depression, 5000	1.1488	0.113	507
	1.3414	0.130	516
	2.0599	0.193	533
	2.2219	0.209	532
Phenol Mol. depression, 7500	1.2793	0.337	284
	2.3011	0.608	283
	2.7735	0.744	279

TABLE II.—BOILING POINT METHOD.

Solvent used	Grams of acid in 100 grams of solvent.	Rise of the B. P. Degrees.	Corresponding mol. wt.
Pyridine. Mol. elevation, 3010	1.1055	0.157	212
	1.2006	0.195	185
	1.6625	0.238	210
Acetic acid. Mol. elevation, 3900	0.8154	0.138	230
	1.5846	0.270	229
Benzene. Mol. elevation, 2670	0.5137	0.041	341
	1.0284	0.077	356
	2.0824	0.147	378
Alcohol. Mol. elevation, 1150	1.1202	0.038	336
	2.2649	0.074	360

Having thus failed in the production of salts of this nature, the preparation and analysis of the abietates of the metals was next taken up, a description of which follows.

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[1] *Monatsh.*, **15**, 636 (1894).

Salts of Abietic Acid.

Assuming that abietic acid, whose composition may be expressed by the formula $C_{20}H_{30}O_2$, is a monobasic acid, the abietates ought to occur as compounds of the type $M(C_{20}H_{29}O_2)n$, where M represents the metal having a valence of *n*. While the latter formula has generally been assigned to the salts, it appears from the following work that the normal salt, $M(C_{20}H_{29}O_2)n$, is rarely formed. On the contrary, acid salts or salts expressed by the general formula, $M(C_{20}H_{29}O_2)n.XC_{20}H_{30}O_2$, are most frequently obtained.

The abietates of sodium, potassium, silver, copper, calcium, barium, strontium, cobalt, nickel, iron, zinc, chromium, aluminum, manganese, cadmium and tin were prepared as described below. The sodium and potassium salts were first made by neutralizing the acid with a slight excess of alkali in a moderately dilute aqueous solution. The reaction took place in a flask provided with a reflux condenser, the contents being heated until complete solution of the acid had been effected. The two salts were also obtained by neutralization of the acid in alcoholic potash or soda solution. Sodium abietate crystallized in long, needle-shaped crystals from the alcoholic solution on cooling.

The abietates of the heavy metals were then prepared from sodium abietate by double decomposition in the following manner: A dilute aqueous solution of sodium abietate was added in small portions to a dilute solution of some salt, usually the chloride or sulphate of the metal whose abietate was desired. By this treatment the abietate is completely precipitated. The latter was then thoroughly washed with water, filtered, and dried in a vacuum at about 80°. To make certain that no hydroxide of the metal present is mixed with the abietate, the dry precipitate was redissolved in pure benzene, filtered, the solvent evaporated, and the residue dried as before. The hydroxide referred to may be formed by the interaction of the inorganic salt and the slight excess of sodium hydroxide present in the sodium abietate solution.

Tin abietate was prepared by double decomposition in a non-aqueous solution. Thus, on adding a benzene solution of stannic chloride to a dilute solution of copper abietate in the same solvent, until no further precipitation of cupric chloride was observed, the abietate of tin remained in solution. After the cupric chloride had settled, the clear, supernatant liquid was filtered and evaporated in a vacuum at about 80°. The residue obtained was redissolved in benzene, filtered, the filtrate evaporated to dryness, and the yellow residue powdered and further dried as before.

It should be stated that the precipitation of the cupric chloride from the reaction between the stannic chloride and copper abietate was *instantaneous*. Reactions of a similar nature were carefully studied several years ago by Kahlenberg,[1] who found that certain salts were precipitated instantaneously and completely in non-aqueous solvents.

Of the salts prepared, the sodium abietate was the only one obtained in a crystalline condition when it was made in an alcoholic solution. The alkali and ammonium abietates have all been isolated in a crystalline form by several investigators, such as Maly,[2] Mach,[3] Levy,[4] Loos,[5] and others.

Since the abietates of the heavy metals, prepared as described, were not crystallizable from solution, their state of purity is doubtful. Although the abietates of the heavy metals have been obtained both as normal and acid salts by Maly,[6] Mach,[7] and others, the results of the analysis given below show that these salts contain an excess of abietic acid in nearly every case.

The analysis of the abietates consisted in finding the percentage of metal present. The substance was carefully ignited in a porcelain crucible until the acid had been burned off. The basic residue was then treated with nitric or sulfuric acid, dried, ignited to constant weight, and weighed as the oxide or sulfate of the metal in question. The following table contains the results of the analyses conducted in this manner, accompanied by the calculated formula in each case:

Tin abietate gave an average of 6 10% tin, which corresponds to $Sn(C_{20}H_{29}O_2)_2.4C_{20}H_{30}O_2$.

Column I contains the results obtained by analyzing abietates which had been prepared by precipitation from aqueous solutions without subsequent solution in benzene. The sodium abietate from which the abietates were made contained a very slight excess of alkali. Column II shows the results from portions of the same samples of abietates as in Column I, with the only difference that they were first dissolved in benzene, the solution filtered and evaporated to dryness, and the powdered residue dried in the usual way before the analysis. As already stated, the benzene treatment was applied in order to remove from the abietate any metallic hydroxide which may have been formed during the precipitation. Hence, the figures in Column II should show a smaller percentage of metal than those in Column I. This is also the case throughout.

The abietates whose analysis is given in Column III were obtained by precipitation from a freshly prepared aqueous solution of sodium abie-

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[1] *J. Phys. Chem.*, 6, 1 (1902).

[2] *Ann. Chem.*, 129, 97 (1864).

[3] *Monatsh.*, 15, 633 (1894).

[4] *Z. angew. Chem.*, 18, 1739 (1905).

[5] *Dissert.*, 1900.

[6] *Ann. Chem.*, 129, 98 (1864).

[7] *Monatsh.*, 15, 633 (1894).

TABLE III.

Salt.	I.		II.		III.	
	% metal.	Corresponding formula.	% metal.	Corresponding formula.	% metal.	Corresponding formula.
Chromium abietate	3.38	$Cr(C_{20}H_{29}O_2)_3.2C_{20}H_{30}O_2$	2.83	$Cr(C_{20}H_{29}O_2)_3.3C_{20}H_{30}O_2$	4.50	$[Cr(C_{20}H_{29}O_2)_3]_3.2C_{20}H_{30}O_2$
	3.20		2.78		4.27	
	3.25		...		....	
Manganese abietate	4.85	$[Mn(C_{20}H_{29}O_2)_2]_2.3C_{20}H_{30}O_2$	4.20	$Mn(C_{20}H_{29}O_2)_2.2C_{20}H_{30}O_2$	6.87	$[Mn(C_{20}H_{29}O_2)_2]_2.C_{20}H_{30}O_2$
	4.94		4.62		6.83	
	4.96		....		....	
Nickel abietate	5.80	$[Ni(C_{20}H_{29}O_2)_2]_6.7C_{20}H_{30}O_2$	5.30	$[Ni(C_{20}H_{29}O_2)_2]_2.3C_{20}H_{29}O_2$	6.94	$[Ni(C_{20}H_{29}O_2)_2]_2.C_{20}H_{29}O_2$
	5.77		5.27		6.98	
	5.75		....		....	
Iron abietate	4.98	$[Fe(C_{20}H_{29}O_2)_3]_2.C_{20}H_{30}O_2$	4.44	$Fe(C_{20}H_{29}O_2)_3.C_{20}H_{30}O_2$	7.45	Basic iron abietate
	5.00		4.44		7.39	
	5.02		....		....	
Cadmium abietate	8.37	$Cd(C_{20}H_{29}O_2)_2.2C_{20}H_{30}O_2$	7 73	$[Cd(C_{20}H_{29}O_2)_2]_2.5C_{20}H_{30}O_2$	10.43	$Cd(C_{20}H_{29}O_2)_2.C_{20}H_{30}O_2$
	8.36		....		11.04	
	8.41		...		....	
Cobalt abietate	6.18	$Co(C_{20}H_{29}O_2)_2.C_{20}H_{30}O_2$	5.80	$[Co(C_{20}H_{29}O_2)_2]_5.6C_{20}H_{30}O_2$	6.38	$Co(C_{20}H_{29}O_2)_2.C_{20}H_{30}O_2$
	6.31		5.73		6.30	
	6.25		....		....	
Strontium abietate	8.26	$[Sr(C_{20}H_{29}O_2)_2]_4.5C_{20}H_{30}O_2$	7.62	$[Sr(C_{20}H_{29}O_2)_2]_2.3C_{20}H_{30}O_2$	6.93	$Sr(C_{20}H_{29}O_2)_2.2C_{20}H_{30}O_2$
	8.21		7.59		7.12	
	8 32		....		....	
Aluminum abietate	3.36	Basic aluminum abietate	2.93	$Al(C_{20}H_{29}O_2)_3$	....	
	3.33		2.97		....	
Copper abietate	8.56	$[Cu(C_{20}H_{29}O_2)_2]_4.C_{20}H_{30}O_2$	6.67	$Cu(C_{20}H_{29}O_2)_2.C_{20}H_{30}O_2$	....	
	8.51		6.78			

tate which contained a considerable excess of alkali, followed by the usual benzene treatment. Consequently, the results in Column III should be about equal to those in Column II. From the table it is seen that this is not the case. Instead of being equal they run higher, and even above those in Column I.

The results of these analyses, Table III, show that the abietates examined were not the pure normal or acid salts but probably normal or acid salts combined with varying amounts of abietic acid. The amount of the acid adhering to the salt may perhaps depend upon the concentration and degree of alkalinity of the sodium abietate solution from which the abietates are précipitated. On the whole, the salts are rich in abietic acid, but the analyses of the iron abietate given in Column III and of the aluminum abietate found in Column I indicate basic salts in these two cases. Furthermore, the results on aluminum abietate given in Column II correspond to the normal salt.

Some of the abietates possess characteristic colors resembling those of the corresponding inorganic salts. In the dry state the abietates given below are colored as follows:

Nickel abietate	greenish yellow
Chromium abietate	greenish yellow
Copper abietate	light blue
Cobalt abietate	lavender
Manganese abietate	pinkish white
Iron abietate	light brown
Silver abietate	white at first

turning brown on exposure to light.

The solubility of fourteen abietates in non-aqueous solvents and in water was investigated. The results are given in Table IV. The capital

TABLE IV.—SOLUBILITY.

	Abietate of													
Solvent.	Ba.	Ca.	Sr.	Cu.	Cd.	Zn.	Cr.	Al.	Co.	Ni.	Mn.	Ag.	Fe.	Na.
Pyridine	S	S	S	S	S	S	S	S	S	S	S	S	S	s
Aniline	S	S	S	S	S	S	S	S	S	S	S	S	S	I
Methyl alcohol	s	s	s	s	S	s	s	I	s	s	s	I	I	S
Ethyl alcohol	s	S	s	s	S	s	s	I	s	s	s	I	s	S
Amyl alcohol	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Benzene	S	S	S	S	S	S	S	S	S	S	S	S	S	I
Turpentine	S	S	S	S	S	S	S	S	S	S	S	S	S	I
Heptane	I	S	S	s	S	S	s	S	s	s	S	I	I	I
Kerosene	I	s	s	S	S	S	s	S	S	S	S	s	I	I
Carbon bisulfide	S	S	S	S	S	S	S	S	S	S	S	S	S	I
Ether	s	S	S	S	S	S	S	S	S	S	S	s	s	s
Acetone	I	s	I	S	S	S	S	I	S	S	S	s	s	I
Carbon tetrachloride	S	S	S	S	S	S	S	S	S	S	S	S	s	I
Chloroform	S	S	S	S	S	S	S	S	S	S	S	S	s	I
Ethyl acetate	S	S	S	S	S	S	S	S	S	S	S	S	s	I
Water	I	I	I	I	I	I	I	I	I	I	I	I	I	S

letter S indicates a fairly copious solubility, namely, that about 4% of the salts are present in solution, while small s represents a very slight solubility. Likewise, the capital letter I means that the salt is practically insoluble. Although these results are only qualitative, they may be of interest to those working with resins.

Based on this table, the following summary concerning the solubility of the salts is added. The abietates of the heavy metals are insoluble in water and but slightly soluble in methyl alcohol. In general, they are quite soluble in the ordinary non-aqueous liquids. Sodium abietate, on the contrary, dissolves readily in water and the alcohols but not in other solvents. Of the three alcohols used, amyl alcohol is the best solvent and methyl alcohol the poorest. Amyl alcohol dissolves all the abietates given in Table IV. Aluminum abietate is insoluble and chromium abietate soluble in acetone. Benzene, turpentine, pyridine, aniline, and carbon bisulfide dissolve all the abietates except that of sodium. Cadmium abietate dissolves in all the non-aqueous solvents tried. Methyl alcohol and heptane are the poorest organic solvents for the abietates.

In this paper it has been shown that abietic acid can be prepared sufficiently pure to give a fairly constant, though not a sharp melting point; that the formation of well defined crystals of the acid is good reason for regarding it as pure; that the production of pure salts of the acid is more difficult than the isolation of the pure acid itself.

Summary.

1. Pure abietic acid was isolated from commercial colophony by alcoholic extraction and recrystallization.

2. The molecular weight of the acid was determined by the freezing- and boiling-point methods. According to the cryoscopic method the molecular weight varied from 263 to 275, from 507 to 533, and from 279 to 284 in acetic acid, benzene, and phenol, respectively. Similarly, for the ebullioscopic method, it varied from 185 to 212, from 229 to 230, from 341 to 378, and from 336 to 360 in pyridine, acetic acid, benzene, and alcohol, respectively.

3. The heat of combustion of the melted acid was observed to be less than that for the unmelted, which indicates that the compound is probably oxidized at temperatures near its melting point. This accounts for the lack of sharpness in the melting point of the acid. The melting point was found to lie between 150° and 152°.

4. The abietates of sodium and potassium were made by neutralizing the acid with the corresponding alkali. From the sodium abietate solution the abietates of the heavy metals were precipitated.

5. Most of the abietates prepared were analyzed and nearly all of them were found to contain an excess of abietic acid.

6. It was observed that the abietates of the heavy metals were quite soluble in non-aqueous solvents and insoluble in water.

In conclusion, the writer takes this opportunity to thank Professor Kahlenberg for his valuable suggestions offered during the progress of the work.

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THE USE OF PYRIDINE AS A SOLVENT IN THE ESTIMATION OF HYDROXYL GROUPS BY MEANS OF ALKYL MAGNESIUM HALIDES.

BY ARTHUR P. TANBERG.

Received December 18, 1913.

During the past eight or nine years there have been published a number of articles dealing with a method for the determination of hydroxyl groups in organic compounds by means of the Grignard reagent. The reaction involved, discovered by Grignard and Tissier,[1] and first developed qualitatively by Tschugaeff,[2] is as follows:

$$R.MgX + R'.OH = R.H + R'.OMgX.$$

In the methods proposed for the quantitative estimation of hydroxyl groups, the substance is dissolved in some solvent and the solution mixed with a solution of CH_3MgI in amyl ether, with a resultant evolution of methane, the volume of which is measured. From this volume can be readily calculated the number of hydroxyl groups in the molecule.

It is necessary, in carrying out a determination, to avoid all traces of moisture in the apparatus and in the reagents used. A more troublesome difficulty arises in connection with the use of a suitable solvent. The requirements in this direction call for, first, low vapor pressure; second, ease of purification; and third, general applicability.

Ethyl ether, the solvent used by Tschugaeff,[3] is useless for quantitative purposes on account of its very high vapor pressure. The first investigators to apply the method to quantitative purposes were Hibbert and Sudborough, who used amyl ether and phenetole with partial success.[4] These two solvents met admirably the first two requirements named above, but their application was not sufficiently wide, and it was shown that while very accurate results were obtained in many determinations, amyl ether solutions of the aliphatic amines and the lower fatty alcohols gave abnormal results, while phenetole solutions of almost all hydroxyl compounds and amines gave low results.

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[1] *Compt. rend.*, 132, 835 (1900).

[2] *Ber.*, 35, 3912 (1902).

[3] *Loc. cit.*

[4] Hibbert and Sudborough, *J. Chem. Soc.*, 85, 933 (1904); Sudborough, *Ibid.*, 95, 477 (1909); Hibbert, *Ibid.*, 101, 328 (1912).

In investigating the efficiency of the method using pyridine as a solvent, Zerewitinoff[1] obtained normal results with aromatic and aliphatic hydroxyl compounds and amines, including the lower fatty alcohols, the figures in many cases showing a deviation from the theoretical which was surprisingly small, if one bears in mind the comparatively high vapor pressure of pyridine, and the fact that Zerewitinoff used and recommends *technical* pyridine as a solvent, and carried out most of the determinations in air, which is absorbed by CH_3MgI.

In view of the advantages which this author claims for the method, it seemed advisable to try out pyridine as a solvent. The results obtained, however, were very unsatisfactory. Thus, with α-naphthol over twice the theoretical amount of gas was evolved. Since the α-naphthol was of known purity, it was decided to investigate the action of pyridine alone on CH_3MgI. The pyridine used in these preliminary determinations was a high-grade technical pyridine obtained from the Baker & Adamson Company, dried over barium oxide as directed by Zerewitinoff. In a number of blank determinations a considerable amount of a gas, presumably methane, was evolved.

In order to find the source of trouble, the apparatus was first tested out by making a blank determination with amyl ether dried over sodium. There was absolutely no change in volume on mixing the amyl ether with the CH_3MgI, and the difficulty was therefore narrowed down to the pyridine itself, or to impurities which it contained other than moisture.

The following series of determinations was therefore carried out, using various samples of pyridine (described below), and using in all cases an excess of the Grignard reagent. The determinations were carried out at room temperature, and it should be emphasized that in each case the evolution of gas was immediate.

Solvent.	Amount of solvent used. Cc.	Amount of CH_3MgI solution used. Cc.	Volume of gas evolved reduced to N. T. P. Cc.
Pyridine I.......	15	10	38.5
Pyridine II.......	10	5	60.9
Pyridine III.......	10	5	27.6
Pyridine III.......	10	5	29.2

Pyridine I was a sample obtained from Kahlbaum, further purified by fractional distillation and by boiling over barium oxide for twenty-four hours.

Pyridine II was another sample of Kahlbaum pyridine, boiling point 115–117°, dried over barium oxide.

Pyridine III was obtained from the Baker and Adamson Company. It was guaranteed to be free from ammonia, and boiled between 116 and 118°.

The pyridine used in these determinations was carefully protected from moisture throughout the process of purification. All apparatus used was dried for one-half hour at 110°, rinsed out with a current of dry air, and kept in a desiccator until used. All the determinations were carried out in an atmosphere of dry nitrogen. The apparatus used was similar to that described by Zerewitinoff, and the magnesium methyl iodide was prepared in accordance with his directions.

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[1] *Ber.*, **40**, 2023 (1907); **41**, 2233 (1908); **43**, 3590 (1910); **45**, 2384 (1912).

No attempt was made to explain the results given in the above table, which differ so strikingly from those obtained by Zerewitinoff. It is certain, however, that the pyridine used was of a higher grade of purity than the technical pyridine which he used, and it was at least as dry. The fact that Oddo[1] obtained satisfactory results by its use may be due to the fact that he employed magnesium ethyl iodide.

In conclusion, attempts to utilize pyridine as a solvent in accordance with Zerewitinoff's directions have failed completely from a quantitative point of view, not only with the technical product but with the repurified Kahlbaum material. Even with added precautions, pyridine has not been found to be a suitable solvent for use in this method; and it would therefore seems advisable that this method be subjected to further investigation before results obtained by its use are accepted.

The author wishes to acknowledge his indebtedness to H. Hibbert, at whose suggestion this work was undertaken.

SWARTHMORE COLLEGE,
SWARTHMORE, PA.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE ORIGIN OF PURINES IN PLANTS.[2]

BY TREAT B. JOHNSON.

Received November 24, 1913.

In the plant kingdom purines occur as normal constituents of the plant cell, linked to sugar in the nucleic acids, and also in a free condition as stable end products of the metabolism of nitrogen. They are found in certain plants associated with protein in all the organs, apparently, in which protein is synthesized or utilized in plant growth. Regarding the mechanism of the processes of formation, or the chemical nature of the simpler organic compounds, which participate in their syntheses, we have, however, practically no knowledge. The primary object of this paper is to present some interesting data, which are very suggestive of the mechanism of purine formation, and which have led us to undertake some new investigations in this fruitful field.

Every process, which has been applied successfully in the laboratory, for the synthesis of purine compounds, is based upon the general principle that the imidazole ring can be introduced into the pyrimidine nucleus.

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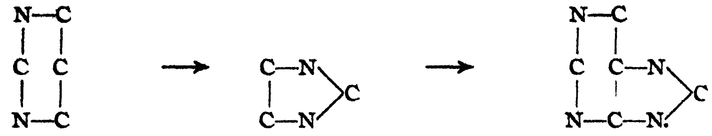
[1] *Ber.*, 44, 2040 (1911).

[2] Pyrimidine Paper LXV.



Pyrimidine. Imidazole. Purine.

This has been effected in different well known ways and it is not necessary to discuss these methods here. The only exception to this general procedure is apparently the observation of Horbaczewski[1] that uric acid is formed in small amount by fusion of urea with aminoacetic acid or the amide of trichlorolactic acid. Gautier,[2] in 1884, claimed to have obtained the purines, xanthine and methylxanthine, by heating hydrocyanic acid with acetic acid and water and expressed the transformation according to the following equation:

$$11\mathrm{HCN} + 4\mathrm{H_2O} = \underset{\text{Xanthine.}}{\mathrm{C_6H_4O_2N_4}} + \underset{\text{Methylxanthine}}{\mathrm{C_6H_6O_2N_4}}.$$

Gautier's products showed a long series of precipitation and color reactions also given by xanthine. This work of Gautier's was repeated, thirteen years later, by Emil Fischer,[3] who showed that the products obtained by Gautier did not give the murexide test and consequently he concluded that they could not be purine compounds. During the following year Gautier[4] replied to Fischer's paper and again discussed the several reactions of his products, which were characteristic of xanthine. He contributed, however, no new experimental evidence to support his conclusions, and, so far as the writer is aware, no further work of Gautier or other investigators, confirming these observations, has since been published.

The reverse process of purine formation, namely, that involving their synthesis from imidazoles or hydantoins by incorporation of the pyrimidine urea nucleus has, so far as the writer is aware, never been accomplished. Attempts to effect such transformations, which have been made in this laboratory,[5] have so far proved unsuccessful. It is of interest to note in this connection that Latham's theory of the formation of uric acid in the animal body is based on the ground, that this purine results by synthesis through the stages of hydantoin and biuret. Uric acid, however, has never been detected in plants, and it has not been definitely established that hydantoin is a naturally occurring compound. The only evidence that hydantoin may occur in plants, which the writer has been able to find, is that given in a paper by Lippmann[6] who writes as follows: "doch

[1] *Ber.*, 15, 2678; *Monatsh.*, 6, 356; 8, 202.

[2] *Compt. rend.*, 98, 1523.

[3] *Ber.*, 30, 3131.

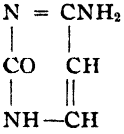
[4] *Ibid.*, 31, 449.

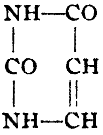
[5] Unpublished work.

[6] *Ber.*, 29, 2652.

sei bei dieser Gelegenheit erwähnt, dass Hydantoin einmal aus dem Safte der bleichen Schösslinge erhalten wurde, die bei feuchtwarmem Wetter in oft erstaunlicher Länge durch das sogenannte 'Auswachsen' der Rüben in den Mieten entstehen und reich an stickstoffhaltigen Verbindungen vershiedener Natur sind.[1] Es bildete kleine weisse Krystalle, deren Schmelzpunkt, der wegen vorherigen Sinterns schwer genau festzustellen ist, bei 214° lag, löste sich leicht in heissem Wasser, besass die Zusammensetzung $C_3H_4O_2N_2$ (gef. 35.85 p. ct. C, 4.17 p. ct. H, 27.88 p. ct. N, 32.10 p. ct. O; ber. 36.00 p. ct. C, 4.00 p. ct. H, 28.00 p. ct. N, 32.00 p. ct. O) und gab mit ammoniakalischem Silbernitrat eine mikrokrystallinische Silberverbindung $C_3H_3O_2N_2Ag + H_2O$." Whether this interesting compound results from the decomposition of allantoin, which has been shown to occur in plants, or is formed by direct synthesis from glycocoll, or is produced by the oxidation of purine compounds, we have no knowledge.

The important fact that purine can be so easily synthesized from pyrimidine compounds is a very strong argument, from a chemical standpoint, that representatives of the latter class of compounds are probably the precursors of purines in plant growth. Several investigators have called attention to this genetic relationship and have suggested that cytosine, I, and uracil, II, may be the two pyrimidines involved in these changes. The close structural relationship between these two pyrimidines and the purines, adenine, III, and xanthine, IV, respectively, for example,


I.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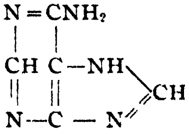
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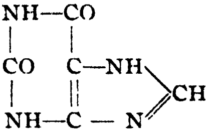
IV.

is surely very suggestive, but notwithstanding this fact, it seems very safe to assume that this relationship will never be of more than theoretical interest, until new methods of converting these two pyrimidines into purines have been developed. Admitting that it is possible to convert pyrimidines of this type into purines,[2] yet, no method has been developed by which purines can be obtained from uracil and cytosine, which still retain the original CO or C-NH_2 pyrimidine groupings in the 6-position of the purine nucleus. These two groupings are characteristic of all the naturally occurring purines. The 3-carbon chain is likewise a characteristic grouping in all naturally occurring purines, and also pyrimidines with the exception of thymine, which contains a methyl group in the

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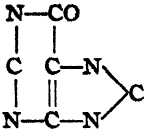
[1] *Z. Rübenz. Ind.*, **35**, 159.

[2] Johns, *Am. Chem. Jour.*, **41**, 59; **45**, 79; *J. Biol. Chem.*, **9**, 161; **11**, 67, 73, 393; **12**, 91; **14**, 1, 299; **15**, 119, 515; **16**, 135.



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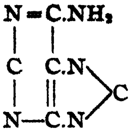
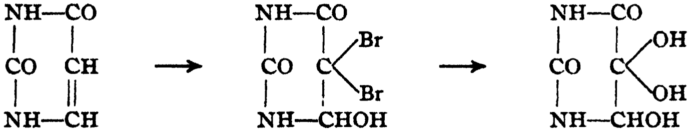


VI.

5-position of the pyrimidine ring. This pyrimidine, therefore, occupies an anomalous position. It is possible that plant enzymes may be found, which are capable of oxidizing uracil and cytosine to isodialuric and aminoisodialuric acids, respectively, but no such transformation has yet been effected in the laboratory by direct oxidation. Wheeler and Johnson[1] have shown that both uracil and cytosine can be converted into isodialuric acid, VIII, but the change involves, first, the formation of the dibromopyrimidine VII, by the action of hypobromous acid and secondly a treatment with alkali to remove the two halogen atoms. The transformation of uracil is represented by the following formulas:



VII. VIII.

It is important to note, furthermore, that the pyrimidines—uracil and cytosine have never been found in a free condition in plants, but always in combination linked as neucleosides.

If now uracil and cytosine are not intermediate stages in the natural syntheses of purines in plants, then what is the mechanism of their formation. In other words, what further evidence have we that pyrimidines may be the precursors of these substances?

It seems to the writer that the interesting results obtained by Ritthausen and coworkers,[2] in his investigations of the extracts of certain plant seeds, are worthy of careful study here, because of the possibility that a correct interpretation of his observations may lead to a definite conception of the mechanism of pyrimidine and purine formation. It is not improbable that we may be able to draw the conclusion from Ritthausen's work, that the changes involved in the natural formation of purines, are analogous to those which take place in the synthetical processes applied in the laboratory.

This investigator isolated from extracts of vetch seeds (*Vicia sativa*) and beans (*Vicia faba and Vicia fabaminor*), by precipitation with mercuric chloride, two characteristic nitrogenous substances, *vicine* and *convicine*, which apparently are closely related to the plant purines.

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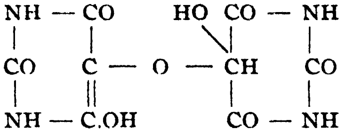
[1] *J. Biol. Chem.*, 3, 183.

[2] Ritthausen and Kreusler, *J. prakt. Chem.*, 2, 333; Ritthausen, *Ibid.*, 7, 334; [2] 24, 218; *Ber.*, 9, 301; 29, 894, 2106; Ritthausen and Preusse, *J. prakt. Chem.*, 59, 487.

Vicine has also been found in beet juice by Lippmann[1] and likewise in vetch seeds and peas (*Pisum sativum*) by Schulze.[2] The latter writes as follows regarding vicine: "Dieser, an seinen Reactionen sehr leicht erkennbare Stoff, findet sich in den ungekeimten Wicksamen in ziemlich beträchtlicher Menge vor." Ritthausen concluded that vicine and convicine are glucosides and assigned to them the formulas $C_{28}H_{47}O_{19}N_{11}.2H_2O$ and $C_{10}H_{15}O_8N_3.H_2O$, respectively. Both compounds are characterized by their behavior on hydrolysis with sulfuric and hydrochloric acids. Vicine is transformed, by heating with 20% sulfuric acid, into *divicine* having the formula $C_4H_7O_2N_4$ (according to Ritthausen),[3] while convicine, on the other hand, is converted, under practically the same conditions, into alloxantine, IX. Ritthausen established the identity of this substance and the alloxantine formed by oxidation of uric acid and states that convicine yields about 36–37% of its weight in this pyrimidine. So far as the writer is aware, this is the only pyrimidine except the three compounds, uracil, thymine and cytosine, which has been found to occur in nature.



IX.

If the formula assigned to convicine by Ritthausen is correct, it is apparent by inspection of the equation below that the change involved in its transformation into alloxantine, by hydrolysis with acids, is not a simple one. The only conclusion that one can draw is that alloxantine

$$C_{10}H_{15}O_8N_3.H_2O = C_8H_6O_8N_4.$$

X.

is not a primary product of the change but is formed by oxidation of a simpler pyrimidine, which is formed as a product of the hydrolysis. If, on the other hand, the molecule of convicine is double that assigned to it by Ritthausen, *viz.*, $C_{20}H_{30}O_{16}N_6.2H_2O$, then alloxantine might be considered a primary product of decomposition, but two of the nitrogen atoms would still be unaccounted for. Ritthausen apparently obtained no evidence of the nature of the secondary, nitrogenous hydrolytic products.

It is a very interesting fact that Ritthausen's formula for convicine corresponds exactly to that for an aminoglucoside of dialuric acid or a glucoside of uramil and its constitution may be provisionally represented by formulas XI or XII.

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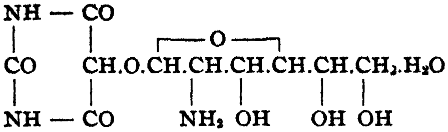
[1] *Ber.*, 29, 2653 (1896).

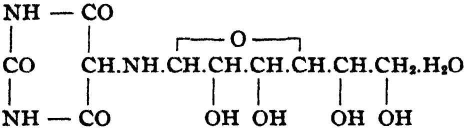
[2] *Z: physiol. Chem.*, 15, 140; 17, 215.

[3] *J. prakt. Chem.*, 59, 482.



($C_{10}H_{15}O_8N_3.H_2O$)

XI.



($C_{10}H_{15}O_8N_3.H_2O$

XII.

The evidence is in favor of formula XI. Theoretically such a combination would be expected to undergo hydrolysis easily with acids giving glucosamine and dialuric acid. When one considers the instability of dialuric acid and the ease with which this pyrimidine undergoes spontaneous oxidation in the air, forming alloxantine, it is at once apparent how the latter compound might be obtained as a final product of the hydrolysis of convicine.

Speculation leads to still more interesting possible relationships, when one comes to study Ritthausen's work on *vicine*. This appears to be a definite compound and Ritthausen's description of its properties is very complete. It dissolved in alkali without decomposition and was precipitated unaltered from such solutions by neutralization with acids. The compound was very stable in the presence of cold alkali, and could even be heated with .dilute barium hydroxide solution without evolution of ammonia. On the other hand, when heated intensely with strong alkali the substance underwent complete decomposition with evolution of ammonia and formation of potassium cyanide. Vicine also dissolved in cold acids without decomposition. Ritthausen wrote as follows regarding these properties:[1]

"Das Studium dieser Zersetzung, und der dabei sich bildenden Produkte, lässt werthvolle Aufschlüse über die Constitution des Vicins erhoffen; leider war es bisher nicht möglich, mich eingehender mit demselben zu befassen." Ritthausen concluded from his early analyses that vicine is to be represented by the formula $C_{28}H_{51}O_{21}N_4$, but decided later[2] that the formula $C_8H_{16}O_6N_3$ is more probably correct. He writes however, as follows: "dass das Molekül grösser als das aus dieser Formel berechnete ist; eine Molekulargewichtsbestimmung konnte aber nicht ausgeführt werden." His final conclusions regarding the constitution of vicine are all expressed in the following statement from his paper:[3] "Bei den

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[1] *J. prakt. Chem.*, **24**, 202.

[2] *Ibid.*, **59**, 480.

[3] *Ibid.*, **59**, 481.

Studien über die Spaltungsprodukte durch Erhitzen mit Schwefelsäure liess sich mit sehr grosser Sicherheit feststellen, dass Zucker in reichlicher Menge entsteht.[1] Vicin demnach als Glucosid zn betrachten ist."

The most characteristic property of vicine is its unique behavior on hydrolysis with 20–30% sulfuric acid. According to Ritthausen it undergoes hydrolysis, when heated with this reagent, giving about 29–30% of its weight in divicine sulfate. This salt was characterized by its insolubility in water, and gave, on analysis, values, from which Ritthausen calculated the formula $2(C_{22}H_{38}O_9N_{20}).5SO_3$. It is very doubtful, however, whether this formula is the correct one.

Divicine was obtained by careful decomposition of its sulfate with the required amount of alkali. It separated in a crystalline condition, but according to Ritthausen, it is not a very stable compound, and gradually undergoes decomposition on exposure to the air, becoming colored dark brown. The base even underwent partial decomposition when crystallized from water. It is a strong reducing agent in aqueous solution and gave, on analysis, results agreeing with the calculated values for a compound having the composition $C_4H_7O_2N_4$. Ritthausen did not suggest a structural formula for this substance, but believed it to be related to allantoin. Attempts to obtain allantoin by oxidation with nitric acid were unsuccessful.

After a critical examination of the analytical values obtained by Ritthausen in his analyses of divicine and its sulfate, and a study of Ritthausen's descriptions of the unique, chemical properties of this base, the writer is forced to the conclusion, that it is not improbable that divicine may be a diaminopyrimidine and that in vicine we may be dealing with a *pyrimidine-nucleoside* combination. The solubility of divicine in alkali and the low percentages of oxygen and hydrogen suggest a cyclic structure and the presence of —CO—NH— groupings in the molecule. Are we dealing here with the precursors of purine nucleosides?

I find that the analytical data obtained by Ritthausen in his analyses of divicine sulfate agree with the calculated values for the sulfate of Traube's[2] 2,6-dioxy-4,5-diaminopyrimidine XIII. In fact, the agreement is perfect for every element except carbon where there is a difference of 4%. Whether there is an error here in Ritthausen's work must be decided by further investigation. The values found and the calculated values for Traube's salt are tabulated below:

Values obtained by Ritthausen.		Calculated for Traube's salt $(C_4H_6O_2N_4)_2H_2SO_4.1^1/_2H_2O$.	
C	27.3	C	23.47
H	3.9	H	4.16
N	27.42	N	27.38
H_2SO_4	24.00	H_2SO_4	23.96

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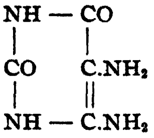
[1] *Ber.*, **29**, 2108.

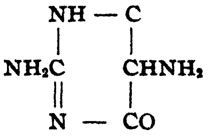
[2] *Ibid.*, **33**, 1382.

Still more interesting is the remarkable fact that the formula for Traube's 2,6-dioxy-4,5-diaminopyrimidine XIII, differs from that, which Ritthausen assigned to divicine by only one hydrogen atom, consequently the theoretical percentages of the elements are so close that it would be extremely difficult to distinguish by analyses alone between the two compounds. These values are tabulated below:

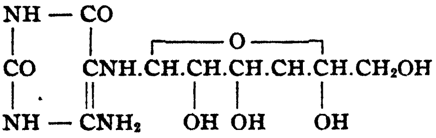
Ritthausen's divicine, $C_4H_7O_2N_4$.		2,6-Dioxy-4,5-diamino-pyrimidine $C_4H_6O_2N_4$.	
C	33.5	C	33.80
H	4.8	H	4.22
N	39 16	N	39.4

2,5-diamino-4,6-dioxypyrimidine XIV, is also to be considered as a possibility.

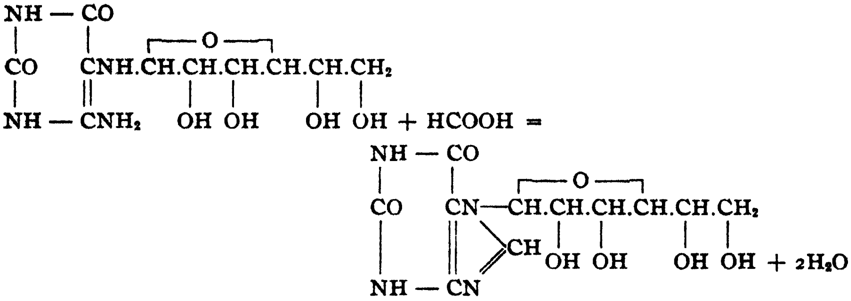

XIII.


XIV.

It is a very significant fact, from a chemical standpoint, that the carbon and nitrogen ratio in divicine is 1 : 1, and this important evidence alone leads to the conclusion that vicine may be a glucoside of 2,6-dioxy-4,5-diaminopyrimidine, which may provisionally be represented by formula XV. Such a constitution would harmonize with the observation of the stability towards alkali and the instability when heated with acids. It would be expected to undergo hydrolysis easily with acid reagents giving 2,6-dioxy-4,5-diaminopyrimidine, XIII, and glucose.


XV.

The compound represented by structure XV, has the empirical formula $C_{10}H_{16}O_7N_4$. Ritthausen assigned to vicine the formula $C_{28}H_{47}O_{19}N_{11}.2H_2O$ and states that the water of crystallization is lost by heating to 160°. If now we take Ritthausen's formula for his anhydrous substance, which is very probably incorrect, and divide by the common factor 2.8, we obtain the expression $C_{10}H_{16.7}O_{6.7}N_4$, surely a remarkable agreement with the formula of the nucleoside of 2,6-dioxy-4,5-diaminopyrimidine $C_{10}H_{16}O_7N_4$. When one considers the fact, that the pyrimidine nucleoside, XV, by condensation with formic acid could undergo transformation into a nucleoside or xanthine hexoside, XVI, it will at once be apparent why the writer is interested in acquiring a better knowledge of Ritthausen's interesting compounds.



XVI.

New investigations are now in progress and we hope to obtain new and important data bearing on these interesting problems.

New Haven, Conn.

[Contributions from the Sheffield Chemical Laboratory of Yale University.]

RESEARCHES ON PYRIMIDINES. LXVI. THE FORMATION OF PYRIMIDINES FROM DIETHYL AMINOMALONATE AND AMINO MALONICNITRILE.

By Treat B. Johnson and Ben H. Nicolet.

Received November 24, 1913.

1. Introduction. 2. Diethyl Aminomalonate and its Derivatives. 3. Experimental Part.

1. Introduction.

In the previous paper[1] the assumption has been expressed that pyrimidines of the barbituric acid series may be the precursors of purines in plant growth, and we discussed new evidence that dialuric acid and uramil may be the representatives of this series, which are involved in these changes. It is easily conceivable how both of these pyrimidines, if formed, might undergo condensations with urea or formamide[2] and be transformed into purine compounds, consequently it is of especial interest to consider how cyclic compounds of this type might be formed in growth from simpler substances.

The question of the relation of hydrocyanic acid to the mechanism of the natural synthesis of purines is an interesting problem, concerning

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[1] Johnson, This Journal, 36, 337 (1914).

[2] It is of especial interest to note here that W. Löb (*Ber.*, 46, 684) has recently reported a synthesis of aminoacetic acid from formamide and water vapor, under the influence of the silent electrical discharge. Oxamide was also formed under the same conditions. The synthesis was therefore a complete one and the apparent course of the reaction was as follows:

$$2HCONH_2 \xrightarrow{-H_2} NH_2CO.CONH_2 \xrightarrow{+H_2O} NH_2COCOONH_4 \xrightarrow{+2H_2} NH_2CH_2COONH_4.$$

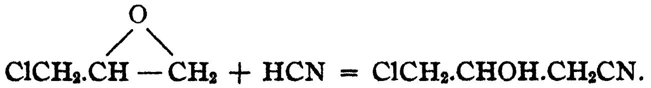
Though the yield of glycocoll was small, Löb considers this the nearest approach yet made to the actual conditions of plant synthesis. It is not improbable that formamide may play an important part in other natural syntheses (T. B. J.).

which practically nothing is known. Throughout the history of this chapter of biochemistry can be traced the feeling, however, that this organic acid, which is known to occur in a free condition in plants, plays a far more important part in these changes than it is customary to assume for it. Adenine, indeed, is a polymeric modification of prussic acid and hypoxanthine is formed easily by simple hydrolysis of this aminopurine. Gautier[1] recognized the biological significance of hydrocyanic acid in nature's processes and in his interesting paper, in which he describes his supposed synthesis of xanthine and methyl xanthine from prussic acid,[2] he writes as follows: "Le méchanisme des synthéses dout je viens de donner l'apercu, me parait trés rapproché, sinon identique, de celui qui se passe chez les végétaux," and also in the same article: "Je dois ajouter en terminant, que ces agrégations d'edifices organiques complexes peuvent se produire même à froid, quoique avec plus de lenteur, sous l'influence des alcalis ou des sels alcalins agissant sur CNH, nouveau rapprochement de ces synthéses avec celles qui se font chez les végétaux." Notwithstanding the fact that Gautier's attempts to synthesize purines from prussic acid were unsuccessful, and that others have been tempted to give too much importance to the protein molecule of hydrocyanic acid, more reasonable syntheses are not wanting.

It is a well known fact that hydrocyanic acid is very susceptible to polymerization, and of all the transformations which it is known to undergo, that in which three molecules unite to form aminomalonic nitrile I,

$$3HNC = \underset{\text{I}}{NH_2CH(CN)_2}.$$

is probably the best understood. Lange[3] was apparently the first to observe this unique transformation while trying to make hydrocyanic acid add to epichlorhydrin. He observed no evidence of the formation of the



$$ClCH_2.CH \overset{O}{—} CH_2 + HCN = \underset{\text{II.}}{ClCH_2.CHOH.CH_2CN}.$$

hydroxynitrile II, but succeeded in isolating a substance having the formula $C_3H_3N_3$. On hydrolysis, this interesting product gave an acid, which evolved carbon dioxide, on heating, and was transformed into aminoacetic acid IV. Its structure, therefore, was established by this observation.

$$\underset{\text{I.}}{NH_2CH(CN)_2} \longrightarrow \underset{\text{III.}}{NH_2CH(COOH)_2} \longrightarrow CO_2 + \underset{\text{IV.}}{NH_2CH_2COOH}.$$

Hörrmann[4] and Lespieau[5] later studied this polymerization reaction of

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[1] *Bull. soc. chim.*, 42, 141 (1884).

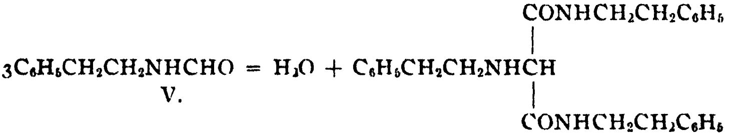
[2] *Loc. cit.*

[3] *Ber.*, 6, 99 (1873).

[4] *Ibid.*, 12, 23 (1879).

[5] *Compt. rend.*, 127, 965 (1898).

Lange's and obtained the desired addition product namely, γ-chloro-β-hydroxybutyronitrile II, without observing the formation of any aminomalonic nitrile. The observation, of Lange was confirmed in 1874 by Wippermann.[1] This investigator found that this characteristic polymerization was greatly favored by small quantities of alkaline salts, especially the cyanide, hydroxide or carbonate of potassium, sodium and ammonium. He also confirmed the aminomalonic nitrile structure, which was already made probable by the results obtained by Lange. Lescoeur and Rigaut[2] likewise investigated the catalytic effect of potassium cyanide on prussic acid, but added little to what was already known. The latest work on the polymerization of the acid is that of Bamberger and Rudolf,[3] who were finally able to describe a method for the preparation of the nitrile which gave over 50% of the theoretical yield. Here again, however, the result was entirely unexpected, being noticed in the course of an unsuccessful attempt to add hydrocyanic acid to dimethylaniline oxide. Whether the function of the aniline oxide is a catalytic one is not known. It is interesting to note, also, in this connection that a reaction, somewhat similar to this characteristic polymerization of hydrocyanic acid, has recently been described by Decker and Becker.[4] They observed, for example, that formylphenylethylamine, V, when heated with phosphorus pentachloride, is transformed into phenylethylaminomalondiphenylethylamide, VI, with evolution of water.



$$3C_6H_5CH_2CH_2NHCHO = H_2O + C_6H_5CH_2CH_2NHCH(CONHCH_2CH_2C_6H_5)_2$$

V. VI.

This most interesting and long known fact that prussic acid is so susceptible to polymerization, under the influence of specific reagents, suggests that the same transformation of the acid may likewise take place under catalytic influence in nature. The aminomalonic nitrile, if formed, would then be a combination favorable for further syntheses. Theoretically it might lead to pyrimidine combinations in two ways, namely, either condense with urea in a manner analogous to that of malonic nitrile, which was investigated by Traube,[5] or undergo saponification to the corresponding acid and then condense with urea to give uramil. The further condensation of a diaminopyrimidine, VII, or uramil, IX, with urea are reactions requiring no special justification. The complete synthesis of uric acid, for example, from hydrocyanic acid and urea, might theoretically be accomplished according to the stages expressed by the following equations:

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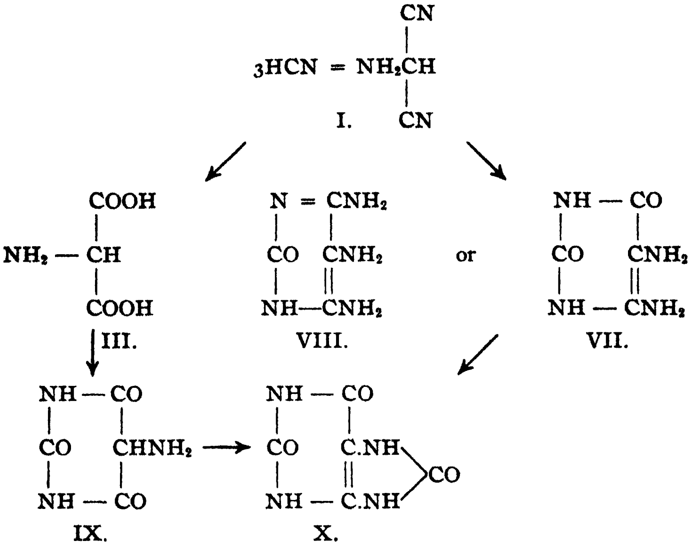
[1] *Ber.*, 7, 767.

[2] *Compt. rend.*, 69, 310 (1879).

[3] *Ber.*, 35, 1082 (1902).

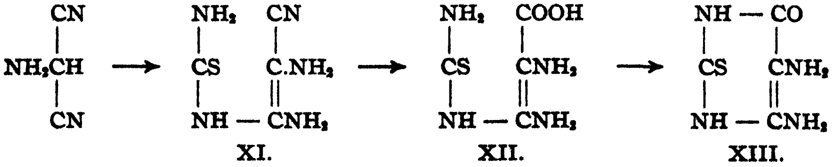
[4] *Ann.*, 382, 369 (1911).

[5] *Ibid.*, 331, 80 (1904); Wheeler and Jamieson, *Am. Chem. J.*, 32, 342.



We have now prepared aminomalonic nitrile I, according to Bamberger and Rudolf's directions and find that it condenses with thiourea, in the presence of sodium ethylate, forming a pyrimidine. The triaminopyrimidine, however, was not obtained as expected, but Traube's[1] 2-thio-6-oxy-4,5-diaminopyrimidine, XIII. The yield was small, owing to much decomposition. That this diaminopyrimidine is formed is probably due to the fact that the intermediate product of the condensation XI, undergoes hydrolysis, giving the acid XII, which then condenses normally, forming the diaminopyrimidine.

These changes may be represented as follows:



That pyrimidines of this type can easily be converted into purines has been established by the work of Traube[2] and Johns.[3]

Dr. Shephard[4] of this laboratory has shown that uramils and thiouramils can be obtained easily by condensing esters of substituted aminomalonic acid with urea and thiourea. We now find that the substitution of the basic amino group into diethylmalonate does not prevent the condensation of this ester with ureas. The amino ester combined with thiourea giving 2-thiouramil, which has already been prepared from thiourea and diethyl phthalimidomalonate.[1] Descriptions of these condensations, which are of biochemical interest, and of some new derivatives of aminomalonic acid are given in the following chapters of this paper:

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[1] *Ann.*, 331, 75.

[2] *Loc. cit.*

[3] Johns and Hogan, *J. Biol. Chem.*, 14, 299.

[4] THIS JOURNAL, 35, 994.

2. Diethyl Aminomalonate and Its Derivatives.

Aminomalonic acid was first described by Baeyer,[2] in 1864, who obtained it by reducing nitrosomalonic acid with sodium amalgam. He analyzed a number of its salts and found that heat converted the free acid smoothly into glycocoll. The same acid was later made by Piloty and Finckh[3] by hydrolysis of uramil with barium hydroxide, a reaction which von Baeyer had tried in vain. Ruhemann and Orton[4] prepared the acid by alkaline hydrolysis of the amide, as did also Piloty and Neresheimer,[5] in 1906. Lutz[6] in the same year, prepared the acid by action of ammonia on monohalogen derivatives of malonic acid.

The free diethylaminomalonate is unknown. Piloty and Neresheimer[7] prepared the hydrochlorides of both the methyl and ethyl esters. They reduced nitrosomalonic esters, dissolved in ether, with aluminium amalgam, and precipitated the hydrochloride of the amino esters by passing dry hydrochloric acid gas into the ether solution. Ureidomalonic acid, for

$$NH_2CO\ NH\ CH(COOH)_2$$

example, has never been synthesized directly.

For our investigation, we prepared the diethyl aminomalonate according to Piloty and Neresheimer's[7] directions with slight modifications. They recommend the reduction of the nitrosoester in ether solution with aluminium amalgam. The reaction is controlled by the addition of water at a rate just sufficient to keep the amalgam reacting smoothly. The yield obtained is about 51%, but, as they justly remark, the product clings tenaciously to the aluminum hydroxide, which must be extracted repeatedly with ether. This difficulty was found to be so real, and the repeated extraction of the bulky precipitate ($Al(OH)_3$) with ether so tedious without the use of proper apparatus, that a new method of reduction was sought.

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[1] Johnson and Shepard, This Journal, 35, 994.

[2] *Ann.*, 131, 291.

[3] *Ibid.*, 333, 71.

[4] *J. Chem. Soc.* (*London*), 67, 1002.

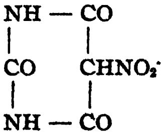
[5] *Ber.*, 39, 514.

[6] *Ibid.*, 35, 2549.

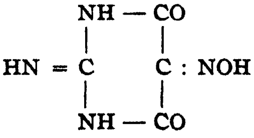
[7] *Loc. cit.*

The reduction was finally accomplished by the use of hydrogen sulfide in alkaline solution. The application of this reducing agent to aliphatic compounds has apparently been very limited, and confined practically to the reduction of violuric acid derivatives.[1] In these cases, hot ammonium sulfide could be used. In the present instance, any excess of ammonia would lead to the formation of the acid amide, and the application of heat would produce hydrolysis. Nitrosomalonic ester[2] was therefore dissolved in water with exactly a molecular proportion of potassium hydroxide, to form the soluble potassium salt. Hydrogen sulfide was then conducted into the cold solution for several hours, and the ester of the aminoacid extracted with ether. It was then isolated in the form of its hydrochloride by saturating the ether with hydrochloric acid gas. An almost pure hydrochloride was obtained in this manner and the yield was 45% of the theoretical. To compensate for the slightly smaller yield than that given by Piloty and Neresheimer,[3] this method is simpler and more convenient, and requires much less attention.

It was found that unless alkali was present, hydrogen sulfide caused no appreciable reduction. An alcoholic solution of ethyl nitrosomalonate gave only a trace of sulfur after saturating with hydrogen sulfide for several hours. This is in accordance with Baeyer's[4] observation that this gas has no action on the neutral water or alcoholic solution of dilituric acid, XIV. On the other hand Traube[5] has reported the remarkable case of the reduction of 2-iminovioluric, XV, with hydrogen sulfide in hydrochloric acid solution.



XIV.



XV.

While nitrosomalonic ester was reduced under the conditions described, diethyl nitromalonate under the same conditions was practically unaffected. This result is the more surprising in connection with the behavior of aromatic nitro and nitroso compounds toward ammonium sulfide. An interesting observation is that of Sachs and Kempf,[6] for instance, who have reported that when 2,4-dinitrobenzaldoxime, XVI, is reduced with an excess of warm ammonium sulfide, the products formed are first 2-nitro-4-aminobenzaldoxime, XVII, and finally, 2,4-diaminobenzaldoxime,

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[1] Traube, *Ann.*, 331, 64.

[2] Bouveault and Wahl, *Compt. rend.*, 137, 196 (1903).

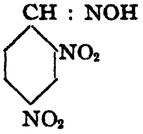
[3] *Loc. cit.*

[4] *Ann.*, 127, 223.

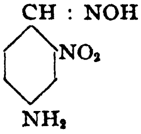
[5] *Ber.*, 26, 2551.

[6] *Ibid.*, 35, 1224.

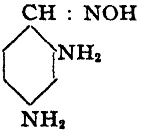
XVIII. This oxime could not be further reduced by this method. The order of stability, therefore, was just the reverse of that found in the aliphatic series.



XVI.

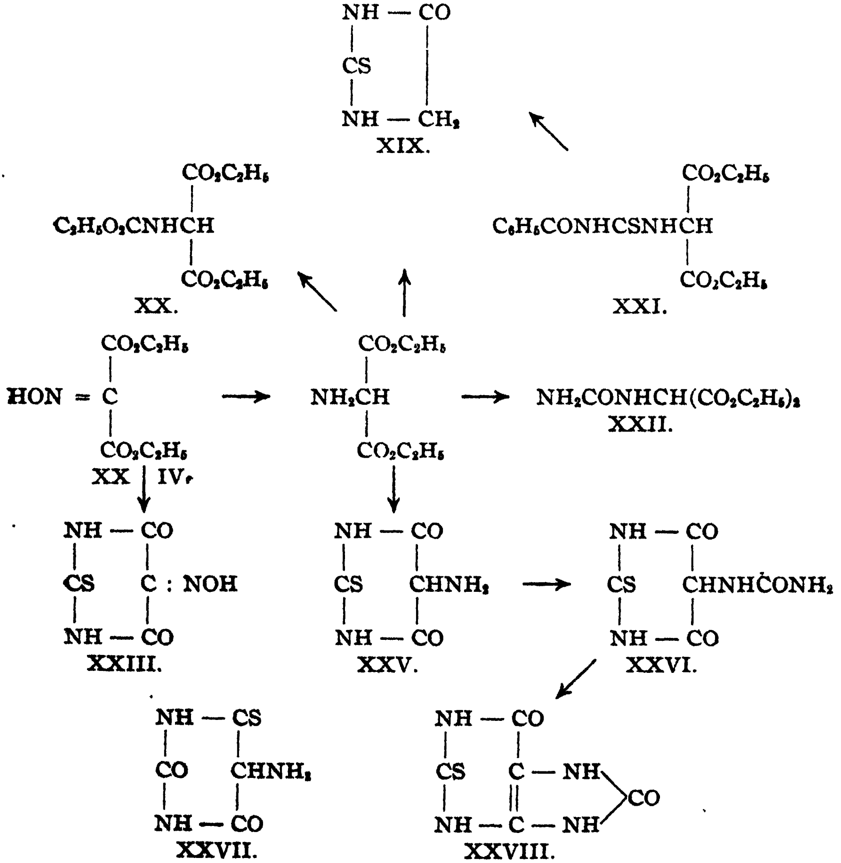


XVII.



XVIII.

As previously stated, diethylaminomalonate was found to show the normal condensation reaction of malonic esters. It condensed with thiourea, in the presence of sodium èthylate, giving a good yield of 2-thiouramil, XXV. The isomeric 6-thiouramil, XXVII, has been prepared by Fischer and Ach[1] and also by Weidel and Niemilovicz.[2] When digested with potassium cyanate solution in the usual way, the thiouramil



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[1] *Ann.*, 288, 157.

[2] *Monats. f. Chem.*, 16, 721.

was converted into 2-thiopseudouric acid, XXVI, which completes the list of possible monothiopseudouric acids. Attempts to close this acid to 2-thiouric acid, XXVIII, either by boiling with hydrochloric acid or by fusion with oxalic acid, were unsuccessful. Fischer and Ach[1] indeed, found the same difficulty with 6-thiopseudouric acid. Johns and Hogan,[1] of this laboratory, have prepared this acid by heating 2-thio-6-oxy-4,5-diaminopyrimidine with urea. Diethyl nitrosomalonate, XXIV, condensed with thiourea giving 2-thiovioluric acid, XXIII.

Since free diethylmalonate is a liquid and its hydrochloride melts with decomposition, it was therefore desirable to obtain characteristic derivatives with definite melting points and small solubilities, that might serve for the isolation and certain identification of small quantities of the ester. The urethane, XX, and the benzoylthiourea ester, XXI, therefore, were prepared and found to serve this purpose well. Either of these compounds can be made and purified from a gram or less of the diethyl aminomalonate. The acylthiourea derivatives on heating with hydrochloric acid are converted into 2-thiohydantoin, XIX.

Diethylureidomalonate, XXII, was easily obtained by the action of cyanic acid on diethyl aminomalonate. An attempt, however, to condense this with urea to form pseudouric acid was unsuccessful. These various changes are represented by the preceding formulas.

3. Experimental Part.

Diethyl Aminomalonate from Diethyl Nitrosomalonate by Reduction with Hydrogen Sulfide.—The diethyl nitrosomalonate was prepared according to the method of Bouveault and Wahl.[2] The crude ester was used for reduction and contained, by analysis, 80% of the pure nitroso compound. The method of reduction was as follows: Ten grams of the nitrosomalonate were dissolved in 30 cc. of water containing 3.0 grams of potassium hydroxide, the solution cooled in an ice bath, and then saturated with hydrogen sulfide gas. Sulfur soon began to separate and after 10 to 12 hours the solution was filtered and extracted repeatedly with ether. This ether extract, after drying with magnesium sulfate, was evaporated, leaving an oil containing diethyl aminomalonate, together with any unaltered diethyl malonate and nitroso ester and some sulfur. This crude oil was finally dissolved in anhydrous ether, filtered from sulfur, and the solution saturated at a low temperature with dry hydrochloric acid gas. The colorless, crystalline hydrochloride of the amino ester separated at once, practically pure. The yield was 4.7 grams, corresponding to 47% of the theoretical. In working up quantities of the nitrosomalonic ester larger than 20 grams, the yield was considerably smaller, probably, on account of the difficulty of getting sufficient hydrogen sulfide absorbed before a part of the ester undergoes hydrolysis.

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[1] *Loc. cit.*

[2] *Compt. rend.*, 137, 196.

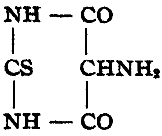
An attempt to prepare the ethyl ester of aminomalonic acid by reduction of diethyl nitromalonate with hydrogen sulfide was unsuccessful. Ten and five-tenths grams of the ammonium salt of the nitro ester, melting with decomposition at 156°, were dissolved in four parts of water, and hydrogen sulfide passed into the solution for 16 hours. As no sulfur had separated during this treatment, a molecular proportion of potassium hydroxide was added, and the gas again conducted into the solution for 16 hours. There was no precipitation of sulfur. On acidifying the solution 0.1 gram of sulfur separated. No diethyl aminomalonate hydrochloride could be obtained from the ether extract, but on passing in ammonia gas, 6.0 grams of the ammonium salt of unaltered diethyl nitromalonate separated.

Diethyl Carbethoxyaminomalonate, $C_2H_5OOC.NHCH(COOC_2H_5)_2$.—To a solution of 3.0 grams of the hydrochloride of diethyl aminomalonate and 5.0 grams of sodium bicarbonate in 25 cc. of water, were added 2.0 grams of ethyl chloroformate in 5 cc. of benzene. The mixture was then shaken as long as carbon dioxide was evolved, and after standing at ordinary temperature for several hours (10) was extracted with ether. The residue obtained after evaporation of the ether crystallized from dilute alcohol in long, colorless needles melting sharply at 63°. The urethane is very soluble in alcohol and ether and slightly soluble in water.

Calculated for $C_{10}H_{17}O_6N$: N, 5.67. Found: N, 5.51.

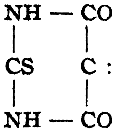
Diethyl Benzoylthioureidomalonate, $C_6H_5CONH.CSNHCH(COOC_2H_5)_2$.—The ester from 2.0 grams of the hydrochloride of diethyl aminomalonate was liberated by adding 0.9 gram of sodium bicarbonate to a solution of the salt in 5 cc. of water. A slight excess of ethyl benzoyldithiocarbamate was then added in 20 cc. of alcohol. The solution was then warmed for an hour on the steam bath, and allowed to stand over night. The alcohol was then evaporated, when the ureido derivative was obtained as a semi-solid substance. This was dried on a porous plate. The yield was 2.9 grams, corresponding to 90% of the theoretical. This compound is readily soluble in warm alcohol and separates, on cooling, in rectangular plates, which melt at 123°. It is moderately soluble in ether and difficultly soluble in water. The ester is converted smoothly into 2-thiohydantoin when digested with hydrochloric acid.

Calculated for $C_{15}H_{18}O_5N_2S$: N, 8.29. Found: N, 8.21.

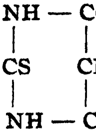
2-Thiouramil,  .—To a solution of 1.0 gram of sodium and 1.5 grams of thiourea in 40 cc. of absolute alcohol were added 3.0

grams of the hydrochloride of diethyl aminomalonate, and the mixture boiled for three hours. The dark red sodium salt which separated was filtered off, dissolved in a little water and decomposed by addition of an excess of acetic acid. The pyrimidine separated as a yellow powder and weighed 1.6 grams, corresponding to 70% of the theoretical yield. It did not melt or decompose below 300°. The compound is very difficultly soluble in the common solvents and was purified by dissolving in alkali, decolorizing by digestion with bone coal, and then precipitating with acid from the hot solution. It was very difficult to remove the inorganic salts carried down with the precipitate.

Calculated for $C_4H_5O_2N_3S$: N, 26.40. Found: N, 25.9.

2-Thiovioluric Acid,  : NOH.—Five grams of crude diethyl nitrosomalonate were condensed with thiourea in absolute alcohol containing 3 molecular proportions of sodium ethylate. After heating for three hours, the gelatinous, dark red sodium salt, which was formed, was filtered off, dissolved in water and the solution acidified, when 0.7 gram of a red powder deposited. This proved to be a mixture of the violuric acid with another product, probably thiobarbituric acid formed from a little malonic ester present in the original nitroso ester. The two were separated by warming with an aqueous solution of sodium bicarbonate; the violuric acid, being a much stronger acid than thiobarbituric, went into solution. On acidifying, the pure 2-thiovioluric acid separated as a yellow powder. It did not melt below 300°. The compound is difficultly soluble in all common neutral solvents. Boiled with water, it gives the latter a yellow color, but without dissolving appreciably. The pyrimidine dissolves in alkali, giving a yellow color.

Calculated for $C_4H_3O_3N_3S$: N, 24.36. Found: N, 24.66.

2-Thiopseudouric Acid,  HNHCONH$_2$.$^1/_2$H$_2$O.—This pyrimidine is formed by warming 2-thiouramil in aqueous solution with potassium cyanate. On acidifying with hydrochloric acid (acetic acid gave no precipitate) the pyrimidine separated as a crystalline powder. The compound is very difficultly soluble in water and alcohol, but readily soluble in alkaline solutions. The pyrimidine deposits practically colorless, but when heated it loses its water of crystallization and becomes deep purple. When heated in a capillary tube it begins, below 200°, to assume a purple color; this becomes very intense until at about 270° it begins to disappear. The color then becomes faintly yellow and remains so until decomposition sets in above 300°. The anhydrous pyrimidine dissolved in alkali giving a deep green solution, which became red when the solution was acidified with acetic acid. The addition of hydrochloric acid discharges the color and produces a precipitate of the pyrimidine.

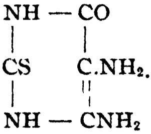
Calculated for $C_6H_6O_3N_4S.{}^1/_2H_2O$: N, 26.48; H_2O, 4.26.
Found: N, 26.34; H_2O, 4.9

Diethyl Ureidomalonate, $NH_2CONH.CH(COOC_2H_5)_2$.—This compound is formed at once when potassium cyanate reacts in a concentrated aqueous solution with the hydrochloride of diethyl aminoacetate. The reaction is complete in 3–4 minutes and the yield of ester is 75% of the theoretical. The urea is difficultly soluble in hot alcohol, from which it crystallizes, on cooling, in octahedra. It melts at 173°.

Calculated for $C_8H_{14}O_6N_2$: N, 12.83, found: N, 12.70.

An attempt to obtain pseudouric acid by condensation of this ester with urea, in the presence of sodium ethylate, was unsuccessful. This is apparently due to the fact that the sodium salt of diethyl ureidomalonate is extremely difficultly soluble in alcohol.

2-Thio-6-oxy-4,5-diaminopyrimidine,



$$\begin{array}{lcl} NH & - & CO \\ | & & | \\ CS & & C.NH_2 \\ | & & \| \\ NH & - & CNH_2 \end{array}$$

.—This pyrimidine was obtained by digesting an alcoholic solution of aminomalonic nitrile with thiourea and the required proportion of sodium ethylate. The alcoholic solution was boiled for 5 hours on the steam bath, and the pyrimidine isolated in the usual manner. It was purified by decolorization of its alkaline solution with bone coal and then precipitating from the alkaline solution with acetic acid. It had no definite decomposition point and after drying to constant weight at 100° a nitrogen determination (Kjeldahl) gave the following result: The yield was small.

Calculated for $C_4H_6ON_4S$: N, 35.40; found: N, 35.60.

NEW HAVEN, CONN.

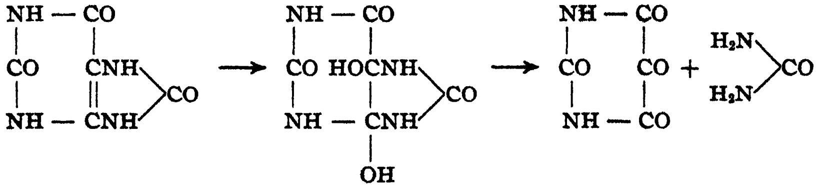
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXVII. SYNTHESIS OF HYDANTOIN-4-CARBOXAMIDE.

BY TREAT B. JOHNSON AND BEN H. NICOLET.

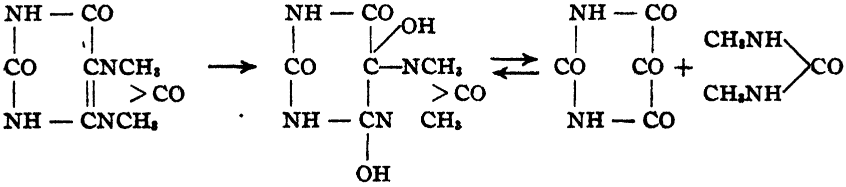
Received November 24, 1913.

The mechanism of the reaction, by which alloxans are formed by the oxidation of uric acids, has been correctly interpreted by Biltz. This investigator has shown, in his recent work on the oxidation of purines, that these transformations (oxidation reactions) involve two independent reactions, namely, a formation of uric acid glycols, by addition of hydroxyl groups at the double bond between the 4 and 5 positions of the purine ring, and finally a dissociation of the glycol into alloxan and urea.[1] The complete oxidation of uric acid, I, to alloxan, III, and urea may therefore, be expressed by the following equation:



I. II. III.

Biltz has also confirmed the earlier observations of Fischer and finds that the stability of the glycols, II, is greatly increased by the introduction of alkyl radicals into the imide groups of the uric acids. Furthermore, he has also made the interesting observation that the same glycols can also be synthesized easily by addition of ureas to alloxans. For example, the dimethyluric acid glycol, V, is formed smoothly by condensation of alloxan with dimethylurea in aqueous and acetic acid solutions. In other words, the transformation of a uric acid glycol into an alloxan and urea is a reversible reaction. Biltz designates this characteristic change as an "Alloxan-Abban" of uric acids.



IV. V. III.

These glycols can also dissociate in an entirely different manner than that represented above. They can undergo what Biltz calls a "Caffolid-Abban." He contributes the interesting observation that the pyrimidine ring is also easily ruptured, under certain conditions, with formation of characteristic hydantoin derivatives. For example, the glycol from tetramethyluric acid, VII, when allowed to stand in aqueous or acetic acid solutions, in transformed smoothly into the 5-hydroxyhydantoylurea, VIII. This compound is, however, unstable in the presence of alkali and undergoes hydrolysis easily, giving a salt of a hydroxyacid, which condenses to the caffolid derivative, IX, when warmed with hydrochloric acid. This characteristic derivative on more intense hydrolysis is transformed into the corresponding acid amide, X, which finally can be converted by reduction with hydriodic acid into the hydantoin derivative, XI. These various changes involved in Biltz's "Caffolid-Abbau" of tetramethyluric acid, VI, may be represented as follows:

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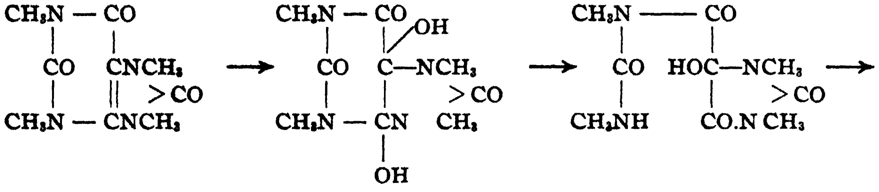
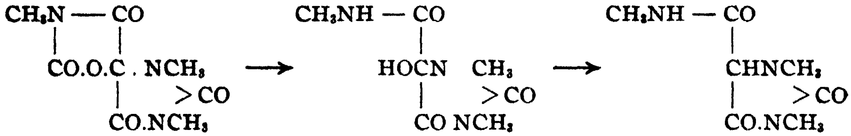
[1] Biltz, *Ber.*, 43, 1589, 1600; Biltz and Krebs, *Ibid.*, 43, 1511, 1618; 44, 282; Biltz and Topp, *Ibid.*, 44, 1511, 1524; Topp, *Inaug. Diss.*, *Kiel* (1911).



$$\begin{array}{l}\mathrm{CH_3N-CO}\\ \quad\mathrm{CO\quad CNCH_3}\\ \qquad\qquad\ \ \mathrm{>CO}\\ \mathrm{CH_3N-CNCH_3}\end{array}\longrightarrow\begin{array}{l}\mathrm{CH_3N-CO\ \ OH}\\ \quad\mathrm{CO\quad C-NCH_3}\\ \qquad\qquad\quad\ \mathrm{>CO}\\ \mathrm{CH_3N-CN\quad CH_3}\\ \qquad\qquad\mathrm{OH}\end{array}\longrightarrow\begin{array}{l}\mathrm{CH_3N-CO}\\ \quad\mathrm{CO\quad HOC-NCH_3}\\ \qquad\qquad\quad\ \mathrm{>CO}\\ \mathrm{CH_3NH\quad CO.N\,CH_3}\end{array}\longrightarrow$$

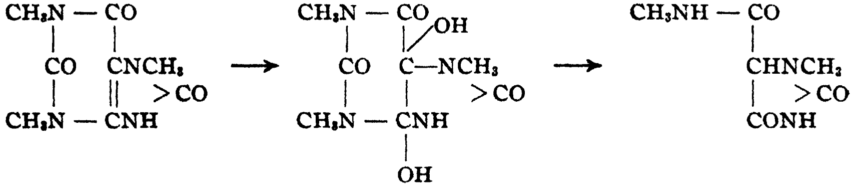
VI. VII. VIII.



$$\begin{array}{l}\mathrm{CH_3N-CO}\\ \quad\mathrm{CO.O.C\,.\,NCH_3}\\ \qquad\qquad\ \ \mathrm{>CO}\\ \qquad\mathrm{CO.NCH_3}\end{array}\longrightarrow\begin{array}{l}\mathrm{CH_3NH-CO}\\ \quad\mathrm{HOCN\quad CH_3}\\ \qquad\qquad\ \ \mathrm{>CO}\\ \quad\mathrm{CO\ NCH_3}\end{array}\longrightarrow\begin{array}{l}\mathrm{CH_3NH-CO}\\ \quad\mathrm{CHNCH_3}\\ \qquad\qquad\mathrm{>CO}\\ \quad\mathrm{CO.NCH_3}\end{array}$$

IX. X. XI.

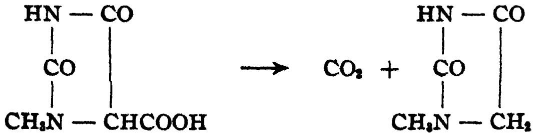
He also applied the same reactions successfully with 1,3,7-trimethyluric acid, XII, and obtained methylhydantoylmethylamide, XIV. This hydantoin is identical with hydrocaffuric acid, which Fischer[1] obtained by reduction of caffuric acid with hydriodic acid.



$$\begin{array}{l}\mathrm{CH_3N-CO}\\ \quad\mathrm{CO\quad CNCH_3}\\ \qquad\qquad\ \ \mathrm{>CO}\\ \mathrm{CH_3N-CNH}\end{array}\longrightarrow\begin{array}{l}\mathrm{CH_3N-CO\ \ OH}\\ \quad\mathrm{CO\quad C-NCH_3}\\ \qquad\qquad\quad\ \mathrm{>CO}\\ \mathrm{CH_3N-CNH}\\ \qquad\qquad\mathrm{OH}\end{array}\longrightarrow\begin{array}{l}\mathrm{CH_3NH-CO}\\ \quad\mathrm{CHNCH_3}\\ \qquad\qquad\mathrm{>CO}\\ \quad\mathrm{CONH}\end{array}$$

XII. XIII. XIV.

Fischer has already shown that this hydantoin undergoes hydrolysis, by heating with barium hydroxide solution, forming methylamine and the barium salt of the corresponding hydantoincarboxylic acid, XV. On decomposing the barium salt with acids carbon dioxide was evolved and methylhydantoin, XVI, was obtained. Fischer[2] writes as follows regarding the stability of this hydantoin acid: "Die freie Säure ist nur in kalter wässeriger Lösung beständig; beim Erwärmen zerfällt sie in Kohlensäure und Methylhydantoin."



$$\begin{array}{l}\mathrm{HN-CO}\\ \quad\mathrm{CO}\\ \mathrm{CH_3N-CHCOOH}\end{array}\longrightarrow\mathrm{CO_2}+\begin{array}{l}\mathrm{HN-CO}\\ \quad\mathrm{CO}\\ \mathrm{CH_3N-CH_2}\end{array}$$

XV. XVI.

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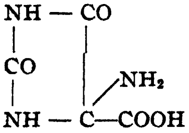
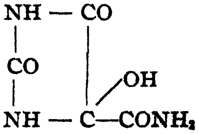
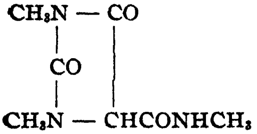
[1] *Ann.*, 215, 282.

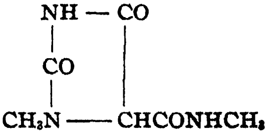
[2] *Loc. cit.*

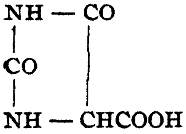
The two methylated hydantoins, XI and XIV, are representatives of a new type of hydantoins and are of especial interest on account of their possible relationship to oxonic acid,[1] $C_4H_5O_4N_3$, an oxidation product of uric acid, whose constitution has not been definitely established. Piloty assigned to this compound the structure represented by formula XVII, but in the light of Biltz's work the isomeric structure XVIII, now appears more probable. These two hydantoins, XI and XIV, are derivatives of the hitherto unknown acid amide of hydantoin 4-carboxylic acid, XX, whose synthesis we now describe in this paper.

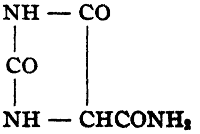

XVII


XVIII.


XI


XIV.

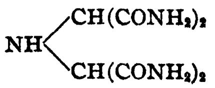

XIX


XX.

The starting point for our research was aminomalonamide, XXI. This acid amide, like the corresponding acid, has been made by a number of investigators. Conrad and Guthzeit[2] obtained it, along with iminodimalonamide, XXII, by the action of alcoholic ammonia on diethyl chloromalonate. Whitely[3] obtained it in the form of its hydriodide by the reduction of nitrosomalonamide with hydriodic acid. Piloty and Neresheimer[4] prepared it by the action of ammonia on the hydrochloride of diethylaminomalonate.

$NH_2CH(CONH_2)_2$

XXI.


$NH{<}\begin{matrix}CH(CONH_2)_2\\CH(CONH_2)_2\end{matrix}$

XXII.

The amide, which we used in our work, was prepared by the reduction of nitromalonamide with aluminum amalgam according to the directions of Ruhemann and Orton.[1] We also employed zinc and formic acid as the reducing agent but obtained formylmalonamide, which has previously been described by Conrad and Schulze.[2] The same formyl compound is also formed by heating aminomalonamide with 85% formic acid. When warmed with barium hydroxide solution aminomalonamide is converted into barium aminomalonate.

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[1] *Ann.*, 333, 91.

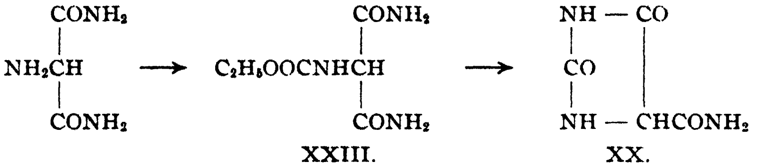
[2] *Ber.*, 15, 605.

[3] *J. Chem. Soc.*, 77, 1040.

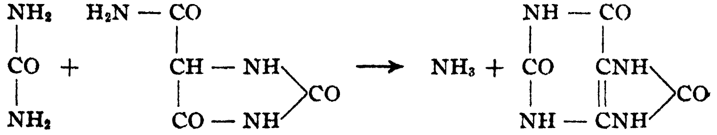
[4] *Ber.*, 39, 514.

We now find that Schotten and Baumann's reaction can be applied successfully with aminomalonamide and ethyl chloroformate, when the urethane represented by formula XXIII is formed in good yield. This interesting compound when treated with an equivalent amount of alkali, either in aqueous or alcoholic solution, undergoes a cyclic condensation, with loss of alcohol, forming hydantoin-4-carboxamide, or according to Biltz's nomenclature "hydantoylamide," XX. This compound is the prototype of the class of hydantoin compounds obtained by Biltz and the first of them to be obtained by direct synthesis. It was hoped that this compound might serve as a basis for the synthesis of caffuric acid and caffolid, but the yield of the amide was too small to make this feasible. Hydantoin-4-carboxamide, XX, is easily hydrolyzed, in the presence of alkali, and transformed into hydantoin.

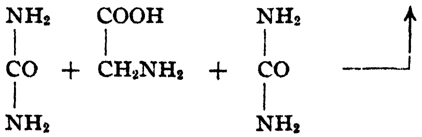
We also investigated the behavior of this amide towards urea. Theoretically it might be expected that a substance of this constitution would condense, when heated with an excess of urea, forming uric acid, XXIV. Attempts, however, to effect such a change were unsuccessful. The negative result is of theoretical interest, however, because it shows that the hydantoin-4-carboxamide, XX, is not an intermediate stage of the reaction when uric acid is formed by heating glycocoll with urea.



XXIII. XX.



XXIV.



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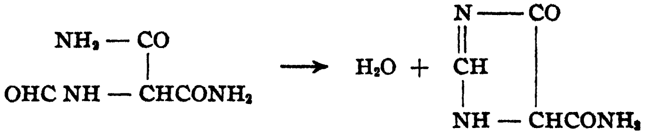
[1] *J. Chem. Soc.*, 67, 1002.

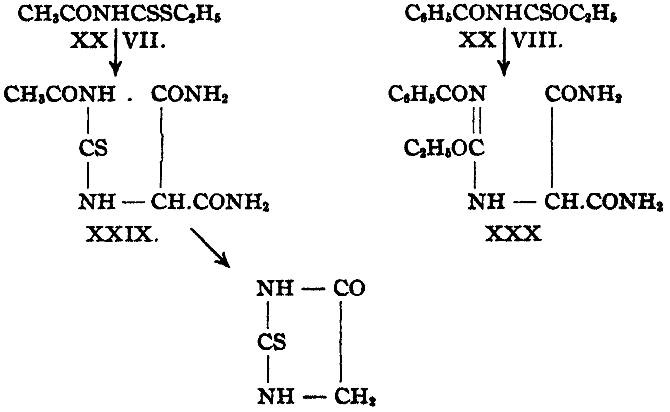
[2] *Ber.*, 42, 729, 735.

Attempts to eliminate water from the formyl derivative of aminomalonamide, XXV, with formation of the glyoxaline compound 5-keto-4,5-dihydroglyoxaline-4-carboxamide, XXVI, were likewise unsuccessful. The amide was heated to 150° with an excess of formic acid, and the sodium salt was also heated for a long time at 180°, but in both cases ofter the treatment of the reaction products with hydrochloric acid, the only definite crystalline product identified was ammonium chloride.



XXV. XXVI.

Aminomalonamide reacted smoothly with cyanic acid giving ureidomalonamide. On warming with barium hydroxide solution this was converted into the characteristic barium salt of ureidomalonic acid, which was obtained by Piloty and Finckh[1] by hydrolysis of pseudouric acid with barium hydroxide. The amide also condensed normally with ethyl acetyldithiocarbamate,[2] XXVII, and ethyl benzoylthioncarbamate,[3] XXVIII, forming acetylthioureidomalonamide, XXIX, and benzoylpseudoethylureidomalonamide, XXX, respectively. The amide, XXIX, when digested with hydrochloric acid was converted smoothly into 2-thiohydantoin, XXXI.



XXVII. XXVIII. XXIX. XXX XXXI.

Experimental Part.

Nitromalonamide, $NO_2CH(CONH_2)_2$.—This amide was prepared according to the method of Ruhemann and Orton.[3] Their directions, however, are not very explicit, and consequently the following details are given. The malonamide was easily obtained in yields of 95% or more according to the directions of Freund.[1] The amide, finely powdered, was added in small portions, with constant agitation, to seven times its weight of fuming nitric acid (sp. gr. 1.5–1.55) kept cool in a freezing mixture. Not more than six grams of the amide should be used in any one preparation, and it was our experience that the addition of this amount to the nitric acid should not occupy more than five minutes. After all the malonamide had been added, the acid solution was quickly poured upon crushed ice, and the nitromalonamide separated quickly by filtration and washed with cold water. Long standing in the acid solution decreased the yield, which under the conditions described varied between 50 and 60%. The pure amide melted with decomposition at temperatures which were easily varied between 168° and 182° according to the rate of heating. Ruhemann and Orton[2] give 172° as the melting point.

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[1] *Ann.*, 333, 71.

[2] Wheeler, Nicolet and Johnson, *Am. Chem. J.*, 46, 456.

[3] *Loc. cit.*

Aminomalonamide, $NH_2CH(CONH_2)_2$.—Our procedure for the reduction of nitromalonamide was as follows: Twenty grams of aluminum turnings were amalgamated and washed free of alkali and mercuric chloride, and covered with 300 cc. of water. Twenty-five grams of nitromalonamide in 75 cc. of 10% aqueous ammonia were then added quickly and the mixture vigorously shaken and cooled to control the reaction, which at first is rather violent. After standing over night to complete the reaction, the solution was filtered, and the aluminium hydroxide triturated with 100 cc. of boiling water and again filtered. The combined filtrates were evaporated to dryness as quickly as possible, when the aminomalonamide, sufficiently pure for subsequent use, was obtained. The yield was 15 grams, corresponding to 75% of the calculated. Aminomalonamide easily undergoes hydrolysis, when warmed with barium hydroxide solution, giving the barium salt of aminomalonic acid. The salt is slightly soluble in cold water and crystallizes from hot water in prisms which do not loose weight when heated at 130°.

Calculated for $C_3H_3O_4NBa$: N, 5.51. Found: N, 5.47.

Formylaminomalonamide, $OCH.NH.CH(CONH_2)_2$.—This derivative, which was obtained by Conrad and Schulze[2] by reduction of nitromalonamide with zinc dust and formic acid, is also easily prepared by heating aminomalonamide at 100° with three times its weight of 85% formic acid. It crystallizes from dilute alcohol in slender, colorless prisms. When heated rapidly in a capillary tube it darkens at 195 200° and melts with effervescence at about 214°.

Calculated for $C_4H_7O_3N_3$: N, 28.97. Found: N, 28.56.

Attempts to transform this formyl compound, by dehydration, into a glyoxaline compound were unsuccessful. In our first experiment, 3.0

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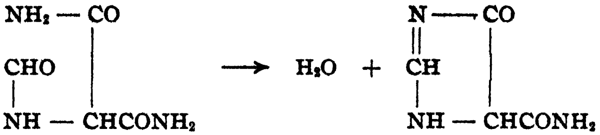
[1] *Ber.*, 17, 133.

[2] *Loc. cit.*

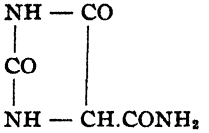


$$\begin{array}{l} NH_2 - CO \\ CHO \\ NH - CHCONH_2 \end{array} \longrightarrow H_2O + \begin{array}{l} N - CO \\ \| \\ CH \\ NH - CHCONH_2 \end{array}$$

grams of aminomalonamide were heated to 150° in a sealed tube, for two hours with six times its weight of 85% formic acid. There was considerable pressure when the tube was opened, and on evaporating the solution a viscous oil was obtained. . The only crystalline product identified, however, was ammonium chloride, which was obtained by triturating the oil with hydrochloric acid. In a second experiment 2.0 grams of the formyl compound were transformed into its sodium salt, and this then heated for one hour in an oil bath at 180°. An examination of the residue did not reveal the presence of any glyoxaline compound. Treatment with hydrochloric acid yielded 1.0 gram of ammonium chloride. There was no evidence in either case that the desired reaction had taken place.

Carbethoxyaminomalonamide, $C_2H_5OOC.NH.CH(CONH_2)_2$.—This compound is easily obtained by application of Schotten and Baumann's reaction with aminomalonamide and ethylchloroformate. The methane is readily soluble in hot alcohol, moderately in cold, and crystallizes in characteristic rosettes of colorless leaflets, which melt at 178°. The compound is practically insoluble in water. The yield was 74% of the calculated value.

Calculated for $C_6H_{11}O_4N_3$: N, 22.2. Found· N, 21 96.

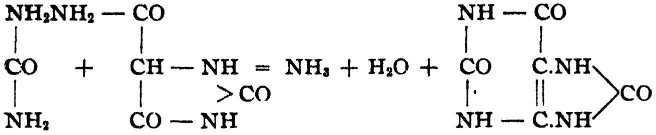
Hydantoin-4-carboxamide, 

$$\begin{array}{l} NH - CO \\ CO \\ NH - CH.CONH_2 \end{array}$$

.—This new hydantoin is formed by the inner condensation of carbethoxyaminomalonamide. The amide was suspended in 20% alcohol containing exactly one molecular proportion of potassium hydroxide. On stirring at ordinary temperature it finally completely dissolved. After standing a few minutes the solution was then warmed to 40° for a few seconds only, filtered from a slight residue, cooled, and then acidified with hydrochloric acid. The hydantoin separated, on cooling, in hexagonal prisms or thin plates, which melted with effervescence at 249°. The hydantoin is very soluble in water, difficultly soluble in alcohol. It was purified for analysis by crystallization from dilute alcohol. The yield of the hydantoincarboxamide was small. The amide group is very easily hydrolyzed in the presence of alkali, and a portion of the amide is transformed into hydantoin. Hydantoin was identified in the filtrates after removal of the carboxamide. The same acid amide is also formed, though in even smaller quantity, by the action of sodium ethylate on the urethane in absolute alcohol.

Calculated for $C_4H_5O_3N_3$: N, 29.38. Found: N, 29.41.

One gram of this hydantoin-4-carboxamide and 3.0 grams of urea were ground together in a mortar, and the mixture heated for about 60–70 minutes in an oil bath at 150°. Ammonia was evolved and the hydantoin was apparently completely decomposed by this treatment. No evidence was obtained of the formation of uric acid.



Ureidomalonamide, $NH_2CONH.CH(CONH_2)_2$.—Three grams of aminomalonamide were dissolved in a solution of 3 cc. of concentrated hydrochloric acid in 12 cc. of water. A saturated aqueous solution of 3.0 grams of potassium cyanate were then added. On allowing the solution to stand for several hours and finally diluting with an equal volume of alcohol, there separated 2.65 grams of ureidomalonamide, or 65% of the theoretical yield. This compound is difficultly soluble in alcohol and moderately soluble in cold water. It crystallizes from dilute alcohol in prismatic crystals (needles) which darken above 200° and decompose at 200–225° with effervescence according to the rate of heating. The amide was not easily freed from potassium chloride, and consequently the determinations of nitrogen were somewhat lower than the theoretical value. The difference in the molecular weights corresponding to the percentages of nitrogen calculated and found is, however, only 5, so that there can be no doubt as to the identity of the compound.

Calculated for $C_4H_8O_3N_4$. N, 35.00. Found. N, 34.00, 34.03.

Barium Salt of Ureidomalonic Acid, $NH_2CONHCH(COO)_2Ba.2H_2O$.—This salt was formed when the above ureidomalonamide was heated with barium hydroxide. One gram of the amide was warmed for one hour at 100° with 2.0 grams of barium hydroxide in 75 cc. of water. Ammonia was evolved and a colorless, crystalline precipitate of the barium salt was formed. This was separated by filtration, washed with hot water and dried for analysis at 100°. The salt is evidently identical with that prepared by Piloty and Finckh[1] from ureidomalonic acid, which was obtained by the hydrolysis of pseudouric acid. The salt contained two molecules of water, which were determined by heating at 130°.

Calculated for $C_4H_4O_5N_2Ba.2H_2O$: H_2O, 10.78. Found: H_2O, 10.83.
Calculated for $C_4H_4O_5N_2Ba.2H_2O$: N, 8.40; Ba, 41.26.
Found: N, 8.35; Ba, 41.28.

Acetylthioureidomalonamide, $CH_3CONHCSNH.CH(CONH_2)_2$. — Two grams of aminomalonamide were added to a solution of 2.8 grams of ethyl acetyldithiocarbamate, $CH_3CONH.CSSC_2H_5$ in 30 cc. of alcohol, and the mixture warmed gently on the steam bath for 24 hours. On cooling, the thiourea separated. The yield was 2.3 grams. The compound is difficultly soluble in both water and alcohol and crystallizes in fine, colorless, hair-like needles. They turned dark when heated above 220°, finally melting at about 254° with strong effervescence.

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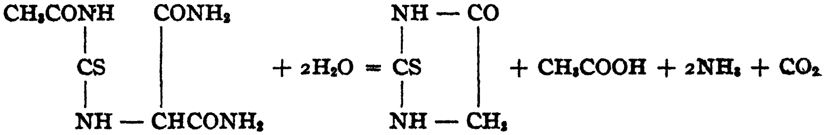
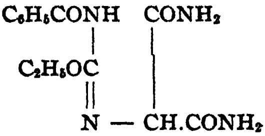
[1] *Loc. cit.*

Calculated for $C_6H_{10}O_3N_4S$: N, 25.64. Found: N, 25.83, 25.14.

Five-tenths of a gram of the above compound was digested for a few hours with an excess of 20% hydrochloric acid. The acid was then evaporated and the residue crystallized from water. Brown prisms separated which melted at 228° with decomposition. This contained sulfur and was identified as 2-thiohydantoin. The hydrolysis of the thioureidomalonamide may therefore be expressed by the following equation:



$$\begin{array}{lll} CH_3CONH \quad CONH_2 & & NH - CO \\ \quad | \qquad\quad\ \ | & & \ \ | \qquad\ \ | \\ \quad CS \qquad\quad | & + 2H_2O = & CS \qquad | \quad + CH_3COOH + 2NH_3 + CO_2 \\ \quad | \qquad\quad\ \ | & & \ \ | \qquad\ \ | \\ \quad NH - CHCONH_2 & & NH - CH_2 \end{array}$$

Benzoylpseudoethylureidomalonamide, 

$$\begin{array}{l} C_6H_5CONH \quad CONH_2 \\ \qquad\quad | \qquad\qquad | \\ C_2H_5OC \qquad\quad | \\ \qquad\ \ \| \qquad\qquad | \\ \qquad N - CH.CONH_2 \end{array}$$

.—One and five-tenths grams of aminomalonamide were warmed for 15 minutes, at 100°, with an equivalent amount of ethyl benzoylthioncarbamate, $C_6H_5CONH.CSOC_2H_5$ in 20 cc. of alcohol. Hydrogen sulfide was evolved, and the pseudourea separated. The compound is difficultly soluble in hot alcohol, from which it separates on cooling in colorless hair-like needles. The compound darkens when heated above 200° and melts at 230–240° with strong effervescence. The compound is very difficultly soluble in water. The yield was 3.0 grams, or 82% of the theoretical.

Calculated for $C_{13}H_{16}O_4N_4$: N, 19.15. Found: N, 19.4, 19.3.

NEW HAVEN, CONN

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON PYRIMIDINES. LXVII. THE CONDENSATION OF THIOUREA WITH ETHYL ALLYLACETOACETATE.

BY TREAT B. JOHNSON AND ARTHUR J. HILL.

Received December 20, 1913.

The behavior of thiourea, urea and guanidine towards diethyl allylmalonate (I), diethyl diallylmalonate (II), and diethyl allylbenzylmalonate (III), has been investigated by Johnson and Hill.[1] With thiourea, no one of the three malonic esters condensed normally, in alcohol solution

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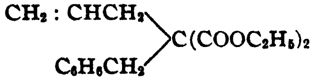
[1] *Am. Chem. J.*, 45, 356; 46, 537.

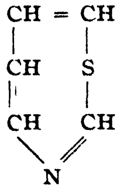
$CH_2:CHCH_2CH(COOC_2H_5)_2$ I. $(CH_2:CHCH_2)_2C(COOC_2H_5)_2$ II.



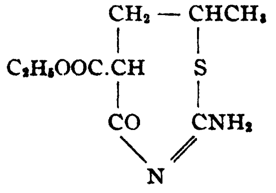
$$(CH_2:CHCH_2)(C_6H_5CH_2)C(COOC_2H_5)_2$$

III.

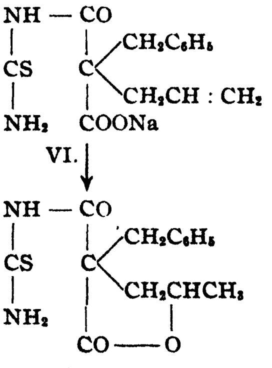
and in the presence of sodium ethylate, giving a thiobarbituric acid compound. The diallylester (II), and the benzylallyl ester (III), condensed, in the presence of sodium ethylate, forming sodium salts of malonuric acids (VI and VII, respectively). When the latter were decomposed by acids, the free malonuric acids immediately underwent isomerization and were transformed smoothly into their corresponding lactones (VIII and IX, respectively). Diethyl allylmalonate, on the other hand, reacted with thiourea in an unique manner giving an excellent yield of an interesting cyclic compound, namely, μ-amino-α-keto-β-carbethoxy-*d*-methyltetrahydrohexathiazole (V). The latter is a representative of a new class of cyclic compounds of which the mother substance would be hexathiazole (IV).



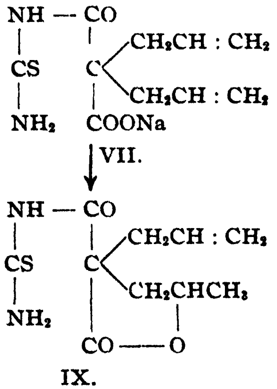
IV.



V.

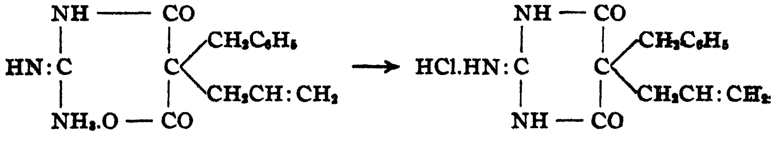


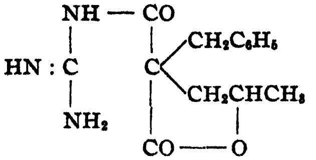
VI. → VIII.



VII. → IX.

While thiourea condensed abnormally in every case, on the other hand, urea condensed normally with all three of the malonic esters, forming barbituric acid compounds. Guanidine also interacted normally with diethyl allylmalonate (I), and diethyl diallylmalonate (II), forming the corresponding pyrimidines. Diethyl allylbenzylmalonate (III), on the other hand, interacted with guanidine giving an inner cyclic salt of a malonuric acid (X). The latter, when treated with acids, was transformed into the hydrochloride of benzylallylmalonylguanidine (XI), with formation of water. There was no tendency, apparently, for the malonuric acid, in this case, to undergo isomerization into the lactone (XII).


X. XI.


XII.

The unique results obtained by interaction of the three allylmalonic esters, I, II, and III, with thiourea were an incentive to examine the behavior of other allyl esters towards this reagent in the presence of sodium ethylate. It was of especial interest to determine, whether the presence of this unsaturated group in β-ketone esters would alter, in any way, the normal behavior of such esters when allowed to interact with thiourea. Ethyl allylacetoacetate is an ester of this type and we, therefore, selected it for this investigation.

We now find that this β-ketone ester reacts smoothly when heated with thiourea, in the presence of sodium ethylate, forming 2-thio-4-methyl-5-allyl-6-oxypyrimidine (XVI). The yield was excellent and we did not obtain evidence of any secondary and abnormal reactions. The sodium salt of this pyrimidine interacted smoothly with methyliodide, forming the corresponding mercaptopyrimidine represented by formula XVII. Both the thio- and mercaptopyrimidines (XVI and XVII, respectively) are converted smoothly into the corresponding oxygen derivative (XVIII), by digestion with chloroacetic acid. This action of chloroacetic acid on mercaptopyrimidines, leading to the formation of oxypyrimidines, is a new reaction and apparently one of general application in the pyrimidine series. 2-Ethylmercapto-6-oxypyrimidine[1] (XX), for example, is converted almost quantitatively, by interaction with this reagent, into uracil (XXI).

2-Methylmercapto-4-methyl-5-allyl-6-oxypyrimidine (XVII) can also be desulfurized by digestion with hydrochloric acid. The oxypyrimidine (XVIII), however, is not the product of the reaction, but the corresponding saturated chloropyrimidine (XIX), which results by addition of the halogen acid at the double bond of the allyl group. The same chloropyrimidine (XIX) is also formed by addition of hydrochloric acid to 2-oxy-4-methyl-5-allyl-6-oxypyrimidine. When 2-thio-4-methyl-5-allyl-6-oxypyrimidine was digested with hydrochloric acid the sulfur was not removed, but the acid added at the double bond in the allyl group, forming the 2-thiochloropyrimidine represented by formula XIV. These various transformations are represented by the following structural formulas:

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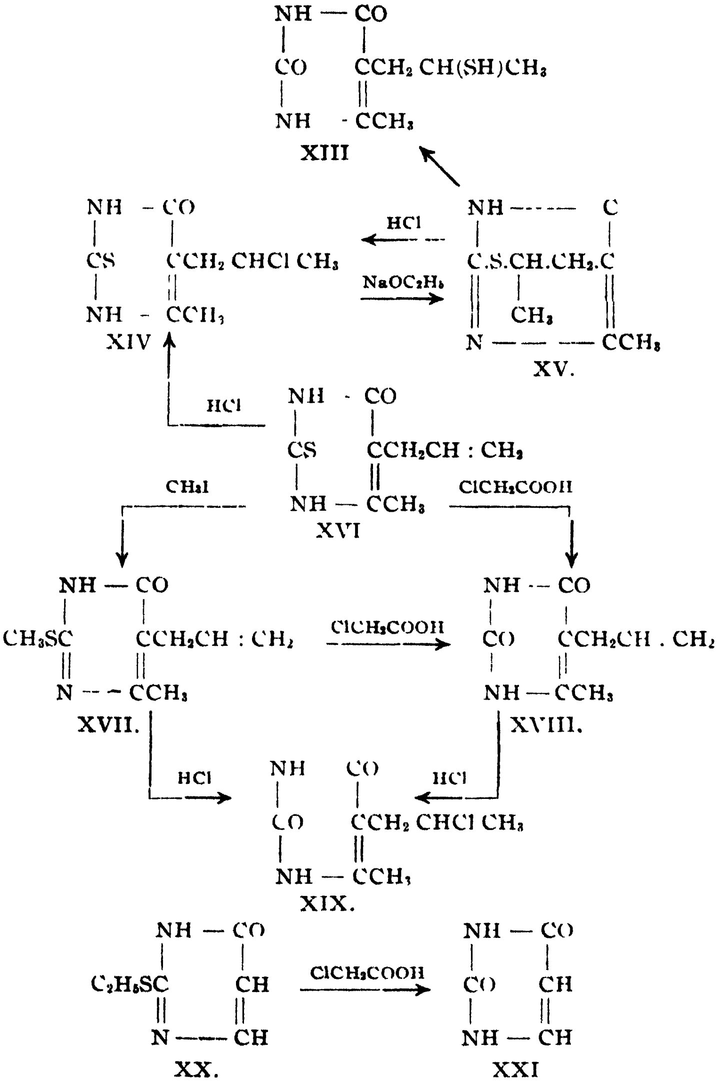
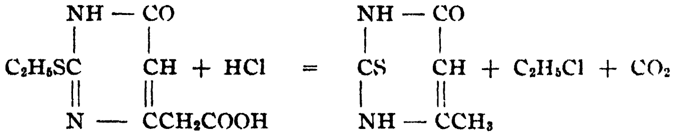
[1] Wheeler and Merriam, *Am. Chem. J.*, 29, 478.



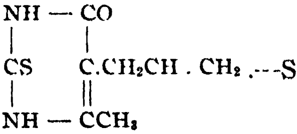
Especially interesting was the behavior of the thiochloropyrimidine (XIV) when dissolved in alcohol in the presence of sodium ethylate. We were able, in this manner, to bridge across from the 2-position to the 5-position of the pyrimidine ring and obtained in excellent yield the cyclopyrimidine represented by formula XV. This interesting compound is the first representative of a new class of pyrimidines and it is our intention to continue their investigation. The cyclopyrimidine reacts in an unique manner when warmed with concentrated hydrochloric acid. They do not interact normally, as might be expected, with formation of an oxypyrimidine containing the mercapto radical in the propyl group as represented in formula XIII, but the bridge dissociates, with cleavage between sulfur and carbon, giving almost quantitatively 2-thio-4-methyl-5-chloropropyl-6-oxypyrimidine (XIV). This is our first observation, in our pyrimidine researches, that a 2-mercaptopyrimidine can be converted directly in its corresponding 2-thio-derivative, by action of hydrochloric acid, at such a low temperature. Wheeler and Liddle[1] were able to convert 2-ethylmercapto-6-oxypyrimidine-4-acetic acid (XXII), into 2-thio-4-methyluracil (XXIII), by the action of hydrochloric acid, but in order to effect the transformation it was necessary to melt the pyrimidine in a stream of dry hydrochloric acid gas, when ethyl chloride and carbon dioxide were evolved.



$$\begin{array}{ccc} NH & - & CO \\ | & & | \\ C_2H_5SC & & CH \\ \| & & \| \\ N & - & CCH_2COOH \end{array} + HCl = \begin{array}{ccc} NH & - & CO \\ | & & | \\ CS & & CH \\ | & & \| \\ NH & - & CCH_3 \end{array} + C_2H_5Cl + CO_2$$

XXII. XXIII.

Experimental Part.



2-Thio-4-methyl-5-allyl-6-oxypyrimidine, $\begin{array}{ccc} NH & - & CO \\ | & & | \\ CS & & C.CH_2CH \,.\, CH_2 \\ | & & \| \\ NH & - & CCH_3 \end{array}$.—Six and seven-tenths grams of sodium were dissolved in 125 cc. of absolute alcohol, and 25 grams of ethyl allylacetoacetate and 13 grams of thiourea were then added. The mixture was heated on the steam bath for ten hours. The reaction was very smooth and the sodium salt of the pyrimidine began to separate within a few minutes' heating. When the reaction was complete, the alcohol was evaporated on the steam bath and the residue dissolved in a small volume of water and the solution acidified with cold, dilute sulfuric acid. Hydrogen sulfide was evolved and the pyrimidine separated as a granular powder. It was soluble in water and alcohol and insoluble in benzene. It was purified for analysis by crystallization from 95% alcohol and separated in flat prisms or rosettes which melted at 187° to an oil without effervescence The compound responded to a test for sulfur and was not desulfurized by digestion with mercury oxide in alcoholic solution. The yield of pure pyrimidine was 15.4 grams.

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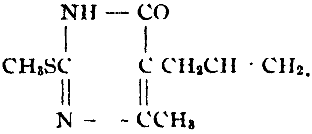
[1] THIS JOURNAL, 30, 1156 (1908).

Calc. for $C_8H_{10}ON_2S$: N, 15.38%; found, 15.40, 15.25, 15.30%. Calc. for $C_8H_{10}ON_2S$: S, 17.58%; found, S, 17.8%.

2-Methylmercapto-4-methyl-5-allyl-6-oxypyrimidine,



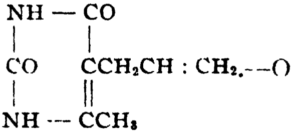
$$\begin{array}{ll} \mathrm{NH} - & \mathrm{CO} \\ | & | \\ \mathrm{CH_3SC} & \mathrm{C\,CH_2CH \cdot CH_2} \\ \| & \| \\ \mathrm{N} - & -\mathrm{CCH_3} \end{array}$$

Five grams of the preceding 2-thiopyrimidine were dissolved in absolute alcohol containing a molecular proportion of sodium ethylate, and 4.5 grams of methyliodide were then added. The solution was heated on the steam bath until neutral in reaction towards turmeric. The alcohol was then evaporated and the pyrimidine washed with water and finally purified by crystallization from alcohol or benzene. It deposited from both solvents in colorless, flat prisms which melted at 189-191° to an oil without effervescence. The pyrimidine is insoluble in water.

Calc. for $C_9H_{12}ON_2S$: N, 14.28%; found, N, 14.30, 14.15, 14.10%.

Action of $ClCH_2COOH$ on 2-Methylmercapto-4-methyl-5-allyl-6-oxypyrimidine.

2,6-Dioxy-4-methyl-5-allylpyrimidine,



$$\begin{array}{ll} \mathrm{NH} - & \mathrm{CO} \\ | & | \\ \mathrm{CO} & \mathrm{CCH_2CH : CH_2} \\ | & \| \\ \mathrm{NH} - & \mathrm{CCH_3} \end{array}$$

—One gram of the mercaptopyrimidine was digested with 5 grams of chloroacetic acid in aqueous solution for 2 hours. The pyrimidine dissolved immediately and methylmercaptan was given off. After the reaction was complete, the solution was cooled, when the above oxypyrimidine separated in a crystalline condition. It was purified by crystallization from alcohol and melted at 218° without effervescence. It gave no test for sulfur.

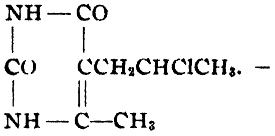
Calc. for $C_8H_{10}O_2N_2$. N, 16.86%; found, N, 16.65%.

This same pyrimidine was also obtained by desulfurization of 2-thio-4-methyl-5-allyl-6-oxypyrimidine. Five grams of the 2-thio compound and 2 molecular proportions of chloroacetic acid (2.8 grams) were dissolved in water and the solution boiled for one hour. The thiopyrimidine dissolved quickly, upon warming, and after three-quarters of an hour the desulfurization was nearly complete, and the oxypyrimidine began to separate from the hot solution. If more than two molecular proportions of the halogen acid were used for desulfurization, the reaction was not as smooth and secondary products were formed, due apparently to further decomposition of the allylpyrimidine. The pyrimidine crystallized from alcohol in characteristic, barrel-shaped prisms which melted at 218° without effervescence. The pyrimidine did not give tests for sulfur and chlorine.

Calc for $C_8H_{10}O_2N_2$: N, 16.86%; found, N, 16.8%.

Action of Hydrochloric Acid on 2,6-Dioxy-4-methyl-5-allylpyrimidine.

2,6-Dioxy-4-methyl-5-(β-chloropropyl)pyrimidine,



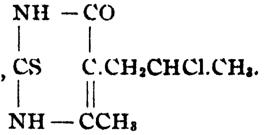
Five grams of the allyl pyrimidine were added to 40 cc. of concentrated hydrochloric acid. It dissolved immediately on warming After heating a short time on the steam bath, the addition of hydrochloric acid at the double bond was apparently complete and the chlorine derivative began to separate from the acid solution. The excess of acid was then removed by evaporation at 100° and the pyrimidine purified by crystallization from water or alcohol. It separated from both solvents in characteristic rosettes of minute prisms. They gave a strong test for chlorine and melted at 233° with decomposition. The pyrimidine is soluble in cold potassium hydroxide solution and is precipitated unaltered by addition of acids. It is insoluble in benzene.

Calc. for $C_8H_{11}O_2N_2Cl$. N, 13 86%; Cl, 17.32%; found, N, 13 8, 13 87%, Cl, 17 01%

This same pyrimidine was also formed by digestion of 2-methylmercapto-4-methyl-5-allyl-6-oxypyrimidine with hydrochloric acid. Six grams of the mercapto pyrimidine were dissolved in 40 cc. of concentrated hydrochloric acid and the solution boiled for one hour, when the evolution of methylmercaptan ceased. The excess of acid was then evaporated and the pyrimidine purified by crystallization from alcohol. It melted at 233° with effervescence. A mixture of this substance and that from the previous experiment melted at the same temperature.

Action of Hydrochloric Acid on 2-Thio-4-methyl-5-allyl-6-oxypyrimidine.

2-Thio-4-methyl-6-oxy-5-(β-chloropropyl)pyrimidine,

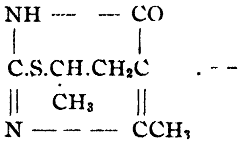


—This pyrimidine was prepared by dissolving 5 grams of the thiopyrimidine in 40 cc. of concentrated hydrochloric acid and evaporating to dryness. After repeating the operation twice, the product was recrystallized from 95% alcohol, when it separated, on cooling, in characteristic ovated prisms which melted at 218–220° with effervescence. The pyrimidine is soluble in alcohol, and difficultly soluble in water and benzene. It dissolved in cold sodium hydroxide solution and was reprecipitated unchanged upon acidifying with hydrochloric acid. The compound gave tests for sulfur and chlorine.

Calc. for $C_8H_{11}ON_2SCl$: N, 12.84%; Cl, 16.0%; found, N, 12.75, 12.70, 12.80%; Cl, 15.74%.

The Action of Sodium Ethylate on 2-Thio-4-methyl-5-(β-chloropropyl)-6-oxypyrimidine.

2,5-Cyclopropylmercapto-4-methyl-6-oxypyrimidine,

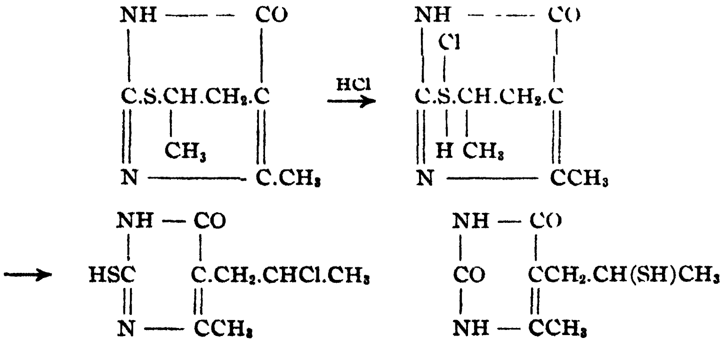


Three grams of the 2-thio-5-chloropropylpyrimidine were dissolved in absolute alcohol containing in solution a molecular proportion of sodium (0.31 gram). Upon heating on the steam bath there was an immediate reaction with separation of sodium chloride. After digestion until the reaction was complete (5 hours) the sodium chloride was separated and the alcohol solution cooled, when the above pyrimidine separated in a crystalline condition. It was purified by crystallization from water or alcohol and separated in characteristic sheaves of needles which melted at 225-227° to an oil. When mixed with the original 2-thiopyrimidine the melting point was lowered to 160°. The cyclopyrimidine is insoluble in cold benzene. It contained sulfur but was absolutely free from chlorine. The yield was excellent.

Calc. for $C_8H_{10}ON_2S$: N, 15.38%; S, 17.58%; found, N, 15.29, 15.10%, S, 17.69%.

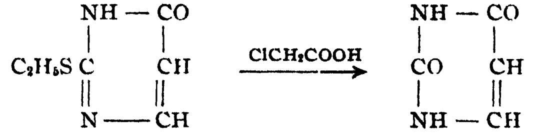
Hydrolysis of the Cyclopyrimidine with Hydrochloric Acid.

One gram of the cyclopyrimidine was suspended in 40 cc. of concentrated hydrochloric acid. On gentle heating the pyrimidine dissolved completely. In a short time a crystalline substance began to deposit from the hot acid solution and there was no evidence of loss of volatile material. After evaporating to dryness, to remove the excess of hydrochloric acid, the substance was purified by recrystallization from 95% alcohol. It separated in the form of ovated prisms, which melted at 218–



220° with effervescence. It gave strong tests for sulfur and chlorine and was identified as 2-thio-4-methyl-5-(β-chloropropyl)-6-oxypyrimidine. A mixture of the hydrolytic product and this 2-thiopyrimidine melted at exactly the same temperature. The mechanism of the reaction may be represented by the preceding formulas. We obtained no evidence of the formation of 2,6-dioxy-4-methyl-5-(β-mercaptopropyl)pyrimidine.

The Conversion of 2-Ethylmercapto-6-oxypyrimidine into Uracil by Digestion with Chloroacetic Acid,



Five grams of the 2-mercaptopyrimidine (m. 152°) and two molecular proportions of chloroacetic acid (5 grams) were dissolved in water and the mixture boiled for one hour. Ethylmercaptan was evolved. After concentration and cooling of the solution 3.0 grams of pure uracil separated while a theoretical yield would have been 3.6 grams. The uracil was absolutely free from sulfur and crystallized in characteristic corpuscular crystals which showed no signs of melting below 300°.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY]

RESEARCHES ON AMINES. IV.[1] THE ALKYLATION AND HYDROLYSIS OF ALIPHATIC SULFONAMIDES. A NEW SYNTHESIS OF SARCOSINE.[2]

BY TREAT B. JOHNSON AND JOSEPH A AMBLER

Received December 20, 1913.

CONTENTS: 1. Hinsberg's Method of Alkylation and its Practical Application. 2. The Application of Hinsberg's Reaction with Aliphatic Sulfonamides. 3. Experimental Work.

1. Hinsberg's Method of Alkylation and its Practical Application.

That sulfonamides possess acidic properties was apparently first observed by Gerhardt and his co-worker Chiozza. The announcement of this characteristic property was made in their paper entitled, "Untersuchungen über die Amide," which was published in 1853.[3] These investigators showed that acid amides are formed by the interaction of amines and acid chlorides. They not only applied this reaction successfully with chlorides of carboxylic acids, but also effected an analogous change with benzene sulfone chloride. They prepared in this manner, by the action of ammonia, benzenesulfone amide, $C_6H_5SO_2NH_2$, and made the important observation that this substance is a strong acid dissolving immediately in alkaline solutions and forming stable salts with the alkali metals and silver. The solubility in alkali of secondary sulfonamides was later observed by Romburgh[1] and Behrend.[2] It is now a well known fact that the solubility of such compounds in alkali is due to the presence in their molecules of the acidic grouping $—SO_2.NH—$. In fact, it is a characteristic property which distinguishes this type of acid amides from the amide derivatives of carboxylic acids. It is of especial interest, however, to note here that acid amides containing the grouping $SO_2.NH$ have been described, which are insoluble in alkali.[3].

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[1] Johnson and Guest, *Am. Chem. J.*, 42, 340; 43, 310; THIS JOURNAL, 32, 761

[2] The Chairman's address, Organic Chemistry Section, 48th meeting A. C. S., Rochester, September 8–12, 1913, comprised the historical and theoretical parts of this paper.

[3] *Ann.*, 87, 299

Following Gerhardt's investigations numerous sulfonamides of all types were synthesized and investigated but apparently, not until about 38 years after the publication of Gerhardt's and Chiozza's paper was the real significance of this property of dissolving in alkali recognized from a synthetical standpoint. In 1891, Hinsberg[4] utilized these compounds for synthetical purposes and published his method of synthesizing secondary amines from primary amines. This is based, as is well known, on two facts, namely, that the alkali salts of sulfonamides easily interact with alkylhalides, in alcoholic solution, giving nitrogen substituted compounds, and secondly, that the latter, when subjected to hydrolysis with acids, are cleaved with formation of amines and a sulfonic acid. His method of alkylation involves no difficult manipulation; the yields of amines are generally very good, and consequently it has met with a wide application.

In the practical application of Hinsberg's method for the synthesis of primary and secondary amines the final operation is to subject the alkylated sulfonamide to hydrolysis with acids in order to cleave the amine from the sulfonyl group. No serious difficulty is generally encountered in effecting this change. It is accomplished generally by heating the amide with concentrated hydrochloric acid under pressure, when the amine is obtained in the form of its hydrochloride, mixed with the sulfonic acid. In order to obtain the free base, the general custom is to make the solution strongly alkaline and then separate the amine by steam distillation or extraction with ether.

The necessity of hydrolyzing the sulfonamides under pressure, however, is disadvantageous for several important reasons. Several attempts have been made by different investigators to hydrolyze with other reagents.

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[1] *Rec. trav. chim.*, 3, 7 (1884).

[2] *Ann.*, 222, 116 (1884).

[3] Solonina, *J. Russ. Phys. Chem. Soc*, 29, 410; *Ibid*, 31, 640; *Chem. Centr.*, 2, 848 (1897); *Ibid.*, 2, 867 (1899).

[4] *Ann.*, 265, 178; Hinsberg and Steupler, *Ibid.*, 287, 220.

Some have been impractical while others perhaps have possessed some advantages over Hinsberg's original method. Marckwald and Huelshoff[1] introduced chlorosulfonic acid (I) as the hydrolytic agent. This chloride reacts with the sulfonamide, on heating, with regeneration of the original sulfonchloride and formation of amidosulfonic acids (II). The free amines are then obtained by digestion of their sulfonic acids with strong alkali when they undergo hydrolysis and the amine is obtained in a pure condition by distillation with steam. The changes involved may be represented by the following equations:

$$C_6H_5SO_2NRR' + \underset{\text{I.}}{HO.SO_2Cl} = C_6H_5SO_2Cl + HOSO_2.NRR'$$

$$\underset{\text{II.}}{HOSO_2.NRR'} + 2NaOH = Na_2SO_4 + H_2O + HNRR'$$

This modification of Hinsberg's method has never received, however, a wide application.

All attempts to hydrolyze the sulfonamides, by heating with alkali, have been unsuccessful. Ullman[2] employed for hydrolysis a mixture of concentrated sulfuric acid and glacial acetic acid. With these reagents he found that a cleavage of the sulfonyl group could easily be accomplished, in those cases investigated by him, by heating the amides with the mixture of acids at 120°. Schroeter and Eisleb[3] later used raw, concentrated sulfuric acid at ordinary temperature, but they found that this acid could not be employed when working with certain aromatic compounds because of the susceptibility of such substances to sulfonation. Their method of hydrolysis, therefore, proved to be of no practical utility, unless sulfanilic acid derivatives were desired as products of the reaction.

The most recent modification of Hinsberg's method of alkylation is that recommended by Witt and Uermenyi.[4] These investigators used strong sulfuric acid as the hydrolytic agent, but employed a different sulfonic acid than that used by Hinsberg. Observing that toluene sulfonic acid is insoluble in strong sulfuric acid at ordinary temperature, they heat the corresponding sulfonamide derivatives with 80% sulfuric acid at 130–150°; when a cleavage of the amide is easily effected. On cooling, the sulfuric acid solution, the toluene sulfonic acid then crystallizes out and can be separated by filtration. The free amine is then obtained by distillation with steam from an alkaline solution. Their modification is, therefore, no improvement whatever over Hinsberg's original method, and involves the same number of operations. On the other hand, there is a very serious objection to using it in the case of aromatic compounds

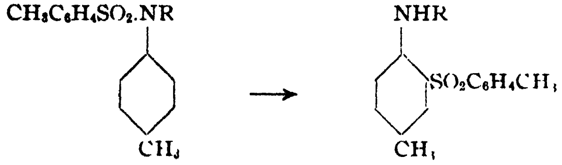
[1] *Ber.*, 31, 3261.

[2] *Ann.*, 327, 104.

[3] *Ibid.*, 367, 101.

[4] *Ibid.*, 46, 296.

because of the tendency of the sulfonamides to undergo molecular rearrangements when heated with sulfuric acid. They are transformed under these conditions into sulfones (III). The extent of these rearrangements varies with the different aromatic amines used.



III

In all the modifications, therefore, which have been recommended as improvements over Hinsberg's original method, resort is always finally made to steam distillation. In fact, it is the only practical method available for separating the amines from the sulfonic acid solution without introduction of other operations and consequently with great loss of the base. There is no apparent advantage in using sulfuric acid as the hydrolytic agent instead of hydrochloric. While steam distillation can generally be applied successfully for the separation of the amines after hydrolysis, on the other hand, there are cases where such an operation would be useless. In the application of Hinsberg's method for the alkylation of amino acids, for example, amphoteric compounds are obtained on hydrolysis which are not volatile with steam. In such cases, the only practical method of separation at present feasible, when benzene sulfone derivatives are used, is precipitation of the amino acids with an alkaloidal reagent. This, however, introduces another operation and furthermore the precipitations are generally not quantitative.

Schotten and Schlömann[1] encountered the difficulty of separating an amino acid from benzene sulfonic acid when working with the corresponding sulfone derivative of amino valerianic acid, $C_6H_5SO_2NH(CH_2)_4COOH$. After hydrolysis with hydrochloric acid, they obtained a stable sulfonic acid salt of the amino acid, $C_6H_5SO_3H.NH_2(CH_2)_4COOH$, which they finally succeeded in decomposing by heating with concentrated hydrochloric acid at 250° in the presence of barium chloride. The sulfonic acid was completely destroyed by this treatment with formation of barium sulfate and benzene. After removal of the excess of barium the amino acid was finally obtained in the form of its hydrochloride by evaporating the solution. This procedure, however, is not of general application because of the danger of decomposing the amino acids by heating with strong acids at such a high temperature.

Johnson and McCollum[2] encountered the same difficulty when an attempt was made to obtain sarcosine from the benzene sulfone derivative of this amino acid, $C_6H_5SO_2N(CH_3)CH_2COOH$. When this compound was hydrolyzed a stable, crystalline sulfonic acid salt was obtained, $C_6H_5SO_3H.CH_3NHCH_2COOH$. In such cases as these, Witt and Uermenyi's[1] modification is apparently applicable and has recently been used successfully by Fischer and Bergmann[2] in the preparation of sarcosine. They have successfully applied Hinsberg's method of alkylation with sulfone derivatives of α-amino acids and find, for example, that the *p*-toluene sulfone derivative of glycocoll, $CH_3C_6H_4SO_2.NH.CH_2COOH$, can easily be converted into the corresponding sarcosine derivative, $CH_3C_6H_4SO_2N(CH_3)CH_2COOH$. When this compound was hydrolyzed with hydrochloric acid the insoluble toluene sulfonic acid was easily separated by filtration and the hydrochloride of sarcosine obtained in good yield by concentration of the acid solution. On the other hand, when the benzene sulfone derivatives were subjected to hydrolysis they were obliged to precipitate the amino acids with phosphotungstic acid in order to separate them from the benzene sulfonic acid. They applied Hinsberg's reaction with the benzene sulfone derivatives of ornithine (IV), and *d*-aminovalerianic acid (VI), and synthesized the corresponding methyl derivatives represented by formulas V and VII.

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[1] *Ber.*, **24**, 3687.

[2] *Am. Chem. J.*, **35**, 54.

$$\begin{tikzcd}
C_6H_5SO_2NHCH_2CH_2CH_2CH(NHSO_2C_6H_5)COOH \arrow[d, "IV"] \\
CH_3NH.CH_2CH_2CH_2CH(NHCH_3)COOH
\end{tikzcd}$$

V.

$$\begin{tikzcd}
C_6H_5SO_2NHCH_2CH_2CH_2CH_2COOH \arrow[d, "VI."] \\
CH_3NH.CH_2CH_2CH_2CH_2COOH
\end{tikzcd}$$

VII.

It is apparent from what has already been presented that the practical utility of Hinsberg's reaction, for amino acid syntheses, would be greatly increased if some method was developed for separating easily the amino acid from the sulfonic acid. If toluene sulfone derivatives are used for experimental purposes this can be accomplished, as is illustrated by Fischer's and Bergmann's synthesis of sarcosine. Toluene sulfone chloride, however, is not always accessible in quantity. The simplest method would be to use a sulfonic acid, which would be easily decomposed by heating with hydrochloric acid. Schotten and Schlömann[1] attempted to meet this condition by heating the benzene sulphone derivative with hydrochloric acid in the presence of barium chloride. Such an energetic treatment, however, is not always permissible. An ideal condition would be that where the hydrolysis could be effected at a temperature below 150° and the complete destruction of the sulfonic acid be accomplished at the same temperature. Furthermore, if the sulfonic acid underwent decomposition giving products, which were volatile with steam, then the hydrochloric acid solution could simply be evaporated to dryness and the hydrochloride of the amine would be the only product left behind. The free base or amino acid could then be separated easily if necessary. Hydrochloric acid could be used as the hydrolytic agent and the whole synthesis of an alkylated amine or amino acid could be accomplished in two operations, namely, *alkylation* and *hydrolysis*. In the following chapter we shall describe a modification of Hinsberg's method of alkylation, which meets all these conditions.

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[1] *Loc. cit.*

[2] *Ann.*, 398, 96.

2. The Application of Hinsberg's Reaction with Aliphatic Sulfonamides.

The aromatic sulfonic acids, which contain the sulfonic rest in the benzene nucleus, are characterized by their great stability in the presence of hydrochloric acid. They can be decomposed by this reagent, however, if heated at a high temperature, and break down, giving sulfuric acid and a hydrocarbon, as expressed by the following equation:

$$C_6H_5.SO_2OH + H_2O = C_6H_6 + H_2SO_4$$

On the other hand, the isomeric sulfonic acids, in which the acid radical is substituted in the aliphatic side chain, are far less stable. These compounds are very unstable at high temperatures and their derivatives, so far as examined, are easily decomposed under conditions where the corresponding aromatic compounds exhibit great stability. For example, Pechmann[1] observed that benzylsulfonyl chloride (VIII) dissociates, on heating, giving sulfur dioxide and benzyl chloride. In fact, the transformation is practically quantitative. Mohr[2] observed that *p*-nitrobenzylsulfonyl chloride, $NO_2C_6H_4CH_2SO_2Cl$, and *p*-brombenzylsulfonylchloride, $Br.C_6H_4CH_2SO_2Cl$, also dissociate in a perfectly analogous manner, forming nitrobenzyl- and bromobenzyl chlorides, respectively, with evolution of sulfur dioxide. Mohr states, in his paper, that the acid chlorides of all benzylsulfonic acids examined, decompose in this manner, and consequently it is difficult, on this account, to obtain them in a pure condition.

$$\underset{\text{VIII.}}{C_6H_5CH_2SO_2Cl} = SO_2 + C_6H_5CH_2Cl.$$

The amides of a limited number of benzylsulfonic acids only have been prepared and, so far as the writers are aware, their behavior on hydrolysis has not been investigated. Pechmann[3] synthesized benzylsulfonylamide, $C_6H_5CH_2SO_2NH_2$, by the action of ammonia on the acid chloride of benzylsulfonic acid, but he gave no description whatever of the chemical behavior of the compound.[1] Mohr prepared the corresponding amide of *p*-nitrobenzylsulfonic acid, but did nothing apparently with the compound. Marckwald and Frahne[2] made the amide of nitro-*o*-hydroxybenzylsulfonic by the action of ammonia on the corresponding sultone and described several of its salts and its methyl ester. Fromme and Palma[3] also studied this type of sulfonamides and prepared Pechmann's benzylsulfonamide by interaction of ammonium carbonate and benzylsulfonyl chloride. They also described the anilide, *p*-toluidide and phenetidide of this acid.

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[1] *Ber.*, **6**, 534.

[2] *Ann.*, **221**, 215.

[3] *Loc. cit.*

As the behavior of this type of acid amides on hydrolysis had not been investigated, it was therefore of special interest to us to determine their chemical behavior when heated with strong hydrochloric acid. We found, to our surprise, that these amides decompose in an unique manner when heated with this reagent. In the first place, they undergo hydrolysis normally, as expected, with formation of the hydrochloric acid salt of an amine. The aliphatic sulfonic (VIII) acid, however, is not obtained

$$C_6H_5CH_2SO_2NHR + H_2O + HCl = \underset{\text{VIII.}}{C_6H_5CH_2SO_3H} + HCl.H_2N.R$$

since it undergoes complete destruction at the temperature of hydrolysis (130–150°). It is not converted under these conditions, however, into a hydrocarbon and sulfuric acid as shown in the case of aromatic sulfonic acids,[4] but is transformed quantitatively into sulfur dioxide and benzyl chloride. Whether this unique change first involves a dissociation of the sulfonic acid into sulfur dioxide and benzyl alcohol, or primarily a formation of the acid chloride and finally a dissociation of the latter is not known. The complete hydrolysis of benzylsulfonamide (IX), with hydrochloric acid, therefore, may provisionally be represented in the following manner:

$$\begin{aligned} C_6H_5CH_2SO_2NH_2 + H_2O &= C_6H_5CH_2SO_2OH + NH_3. \\ NH_3 + HCl &= NH_4Cl. \\ C_6H_5CH_2SO_2OH &= SO_2 + C_6H_5CH_2OH \\ C_6H_5CH_2OH + HCl &= H_2O + C_6H_5CH_2Cl \end{aligned}$$

The products of the reaction are ammonium chloride, and benzyl chloride and sulfur dioxide which are volatile with aqueous vapor. This is apparently a normal reaction, and the yields of amine hydrochlorides are nearly quantitative.

Having established the fact that benzylsulfonamide is decomposed smoothly, by hydrolysis, giving benzyl chloride, sulfur dioxide and ammonium chloride, we next turned our attention to the application of Hinsberg's reactions with this amide. We find that it forms well defined mono-potassium and sodium salts, which react smoothly with alkyl halides, forming the corresponding alkylsulfonamides. In this paper we describe the behavior of these salts towards methyl iodide, benzyl chloride, ethyl brom- and chloroacetates and chloroacetamide.[1] By alkylation of benzylsulfonamide with methyl iodide a mixture of the monomethyl (X), and dimethyl derivatives (XI), is obtained. Attempts were made to decrease the amount of the dimethyl derivative in various ways, but we found that it was always formed in practically constant proportion. Benzyl chloride, however, reacted more smoothly with the monopotassium salt, giving a monobenzyl derivative (XII). When this was subjected to hydrolysis with concentrated hydrochloric acid it was converted smoothly into the hydrochloride of benzylamine (XIII), benzyl chloride and sulfur dioxide.

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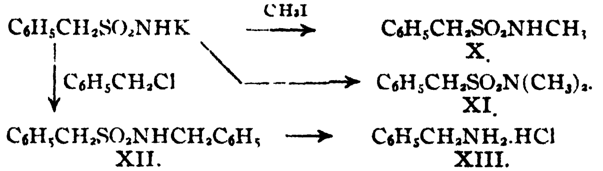
[1] *Loc. cit.*

[2] *Ber.*, 31, 1854.

[3] *Ibid.*, 39, 3308.

[4] Schotten and Schlömann, *loc. cit.*



$$\begin{tikzcd}
C_6H_5CH_2SO_2NHK \arrow[r, "CH_3I"] \arrow[dr] \arrow[dd, "C_6H_5CH_2Cl"] & \underset{\text{X.}}{C_6H_5CH_2SO_2NHCH_3} \\
 & \underset{\text{XI.}}{C_6H_5CH_2SO_2N(CH_3)_2.} \\
\underset{\text{XII.}}{C_6H_5CH_2SO_2NHCH_2C_6H_5} \arrow[r] & \underset{\text{XIII.}}{C_6H_5CH_2NH_2.HCl}
\end{tikzcd}$$

Schotten and Baumann's reaction can be applied successfully with benzylsulfonylchloride and amines. An attempt was made to prepare benzylsulfonglycocoll in this manner, but the amount formed was so small that it was not a practical method of preparation. We also investigated the action of the ethyl esters of chloro- and bromoacetic acids on the potassium salt of the sulfonamide, but here also the reactions were not smooth and a large proportion of the amide was recovered unaltered. We next investigated the action of chloroacetamide on the alkali salts of the sulfonamide and made the interesting observation that they interact smoothly forming benzylsulfonacetamide (XIV). This amide, on digestion with alkalis, was converted quantitatively into the benzylsulfone derivative of glycocoll (XV):

$$C_6H_5CH_2SO_2NHK + ClCH_2CONH_2 = \underset{\text{XIV.}}{C_6H_5CH_2SO_2NHCH_2CONH_2} + KCl$$

$$C_6H_5CH_2SO_2NHCH_2CONH_2 + H_2O = \underset{\text{XV.}}{C_6H_5CH_2SO_2NHCH_2COOH} + NH_3$$

Benzylsulfonaminoacetamide dissolves immediately in alkali and undergoes alkylation smoothly with methyl iodide, forming the amide of benzylsulfonsarcosine (XVI). This same amide is also formed by action of chloroacetamide on the sodium salt of methylbenzylsulfonamide (X). In fact, it was found by experience that the best method of preparation of the amide was to first alkylate benzylsulfonamide with methyl iodide, and then, without isolation of the methyl substitution product, to alkylate finally with chloroacetamide in presence of the required amount of alkali. In this way the desired amide was easily obtained pure in yields of 25–30% of the theoretical. When the amide of benzylsulfonsarcosine (XVI)

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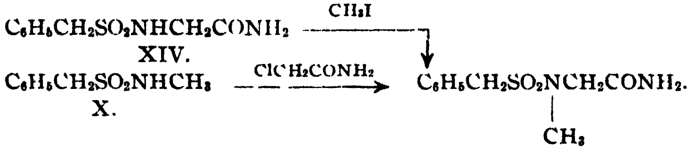
[1] We are continuing this investigation and shall investigate not only the alkylation products of benzylsulfonamide, but also incorporate in our work an investigation of other aliphatic sulfonamides. This type of compounds should be especially valuable for further interesting syntheses. It is not improbable that the potassium salt of benzylsulfonamide may prove as useful for synthetical purposes as the potassium salt of phthalimide (T. B. J.).



$$\begin{tikzcd} C_6H_5CH_2SO_2NHCH_2CONH_2 \arrow[dr, "CH_3I"] & \\ C_6H_5CH_2SO_2NHCH_3 \arrow[r, "ClCH_2CONH_2"] & C_6H_5CH_2SO_2\underset{\underset{CH_3}{|}}{N}CH_2CONH_2. \end{tikzcd}$$

XIV.

X.

XVI.

was digested with barium hydroxide solution it was converted quantitatively into the corresponding acid (XVII). This acid, on hydrolysis with hydrochloric acid, breaks down in a manner perfectly analogous to that in the case of the sulfone derivatives of amines. Sulfur dioxide and benzyl chloride are formed and pure sarcosine hydrochloride (XVIII) is obtained by evaporating the hydrochloric acid solution to dryness. Starting with the amide (XVI), the new synthesis of sarcosine therefore involves three operations and the yields are nearly quantitative at each stage. These changes are represented by the following formulas:

$$\underset{\text{XVI.}}{C_6H_5CH_2SO_2N(CH_3).CH_2CONH_2} \xrightarrow{\text{alkali}}$$

$$\underset{\text{XVII}}{C_6H_5CH_2SO_2N(CH_3)CH_2COOH} \xrightarrow{\text{HCl}}$$

$$\underset{\text{XVIII.}}{CH_3NH.CH_2COOH.HCl} + SO_2 + C_6H_5CH_2Cl$$

The characteristic feature of our modification of Hinsberg's method of alkylation is the fact that the sulfonic acid employed is completely decomposed by heating with hydrochloric acid and consequently renders it possible to obtain the hydrochlorides of the amines or amino acids absolutely free from the sulfonic acid without precipitation with an alkaloidal reagent. Benzylsulfonamide can easily be obtained in any quantity desired. The only unsatisfactory step in the synthesis is that involving alkylation in order to obtain the amide (XVI). Here the yield of purified product is generally at best only 25–30% of theory. Efforts are being made, however, to determine the best conditions for obtaining a maximum yield. New investigations are now in progress, and we shall apply the method for the preparation of other compounds of biochemical interest.[1]

Experimental Part.

Sodium Salt of Benzylsulfonic Acid, $C_6H_5CH_2SO_3Na$.—This salt was prepared according to the method of Fromm and Palma.[2] Two hundred and fifty grams of crystallized sodium sulfite, or 125 g. of the anhydrous salt, in about 200 250 cc. of 10% sodium hydroxide solution were boiled under a reflux condenser with 125 g. of benzyl chloride. After 3–4 hours' boiling the benzyl chloride had practically all disappeared and the hot solution, after diluting with water, was filtered through wet filter papers to remove unaltered benzyl chloride, and also the small amount of benzyl alcohol which is formed in the reaction. On cooling the aqueous solution the sodium salt separated in the form of glistening plates. More of the same salt separated after concentrating the solution. The salt was dried at 100° and used, without further purification, for the following experiments. The yield was about 80% of the theoretical:

Benzylsulfonchloride, $C_6H_5CH_2SO_2Cl$.—This chloride, which has been described by Pechmann, was prepared as follows: 50 g. of powdered, anhydrous sodium benzylsulfonate were mixed in a flask with 54 g. of pulverized phosphorus pentachloride and the mixture then moistened with phosphorus oxychloride. After a few minutes there was an energetic reaction and the flask was immersed in cold water to prevent decomposition of the sulfonchloride. After the violent reaction was over, the mixture was then heated at 70–89° for 4–5 hours. If heated at a higher temperature the sulfonchloride is gradually decomposed, forming sulfur dioxide and benzyl chloride. The semi-solid mass was finally poured into ice-water to decompose the phosphorus halides, when the sulfonchloride separated as a heavy oil, which finally solidified. After filtering and washing with water it was dried on a porous plate to remove traces of benzyl chloride, and finally converted into the acid amide.

Benzylsulfonamide, $C_6H_4CH_2SO_2NH_2$.[3]—The amide is easily prepared by mixing the acid chloride with a large excess of concentrated, aqueous ammonia. The chloride dissolved immediately. After concentration of the solution and cooling, the amide separated in the form of colorless needles. It was purified by crystallization from hot water and melted at 104–105°.

Sodium Salt of Benzylsulfonamide, $C_6H_5CH_2SO_2NHNa$.—This salt separated in a crystalline condition when the solutions of molecular amounts of sodium ethylate and benzylsulfonamide, in absolute alcohol, were united. It is insoluble in ether, very soluble in cold water, and insoluble in cold alcohol. It was dried for analysis at 100°.

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[1] Owing to the departure of Dr. Ambler from this laboratory these researches will be continued by other investigators in our department (T. B. J.).

[2] *Loc. cit.*

[3] Peckmann, *loc. cit.*

Calc. for $C_7H_8O_2NSNa$: N, 7 27%; found, N, 7.06%.

Potassium Salt of Benzylsulfonamide, $C_6H_5CH_2SO_2NHK$.—This was prepared by the action of potassium hydroxide on benzylsulfonamide in absolute alcohol. It separated as glistening, micaceous flakes. After filtering and washing with ether it was dried at 100°.

Calc. for $C_7H_8O_2NSK$: N, 6.71%; found, N, 6 52%.

Methyl Benzylsulfonamide, $C_6H_5CH_2SO_2NHCH_3$.—The potassium or sodium salts of benzylsulfonamide were suspended in absolute alcohol, an excess of methyl iodide added, and the mixture then warmed on the steam bath until the solution gave no alkaline reaction. The alcohol was then evaporated and the residue dissolved in the least possible amount of hot water. On cooling, a colorless solid separated, which was identified as a mixture of the mono- and dimethyl amides. These were separated by means of potassium hydroxide solution, in which the monomethyl amide is soluble. The insoluble dimethyl amide was removed by filtration and the filtrate acidified with hydrochloric acid, when the monomethyl compound separated as colorless needles. The amide is soluble in ether, alcohol and hot water and melts at 109–110° to a clear oil.

Calc. for $C_8H_{11}O_2NS$: N, 7.59%; found, N, 7.63%.

Dimethyl Benzylsulfonamide, $C_6H_5CH_2SO_2N(CH_3)_2$.—The crude dimethyl amide obtained above was washed with potassium hydroxide solution and then purified by recrystallization from hot water and absolute alcohol. It separated in thin plates, which melted at 102–103° to an oil. It was dried for analysis over sulfuric acid:

Calc. for $C_9H_{13}O_2NS$: N, 7.05%; found, N, 7.01, 7.26%.

Attempts were made to increase the yield of the monomethylamide by alkylation under different conditions. The reaction was applied with molecular amounts of the methyl iodide and the sodium or potassium salt of the amide in absolute and 95% alcohol, and also with two molecular proportions of the salts to one of methyl iodide in the same solvent, but in both cases the dimethyl amide was always formed. It was extremely difficult to separate the unaltered amide from the monomethyl derivative.

Molecular quantities of the sulfonamide, methyl iodide and potassium carbonate required for the equation,

$$C_6H_5CH_2SO_2NH_2 + CH_3I + K_2CO_3 = C_6H_5CH_2SO_2NHCH_3 + KI + KHCO_3,$$

were warmed in a mixture of two volumes of water to one of 95% alcohol until the methyl iodide had all disappeared, but here, also, the dimethyl as well as the monomethyl amide was formed. The best yield of pure monomethyl amide obtained in any experiment was 35% of the theoretical.

Ethyl Benzylsulfonaminoacetate, $C_6H_5CH_2SO_2NH.CH_2COOC_2H_5$.—This was prepared by digesting the potassium salt of benzylsulfonamide in alcohol with ethyl bromoacetate. After the reaction was complete the alcohol was then evaporated and the ester dissolved in ether and dried over calcium chloride. The ester was obtained as a viscous oil. Its potassium salt was obtained by digesting the ester in alcohol with the required proportion of potassium hydroxide. It separated as a colorless powder and was dried for analysis at 100°.

Calc. for $C_{11}H_{14}O_4NSK$: N, 4.76%; found, N, 4.51, 4.66, 4.46%.

The amount of ester obtained was very small. Attempts to improve the yield were made by boiling molecular proportions of ethyl bromo- and chloroacetate with the potassium salt of the amide in ether and benzene, but after two weeks' digestion a large proportion of the potassium salt was still unchanged. No better results were obtained by employing the silver salt of the amide. An attempt to prepare the ester in quantity by application of Schotten and Baumann's reaction was unsuccessful.

Benzylsulfonaminoacetamide, $C_6H_5CH_2SO_2NHCH_2CONH_2$.—The chloroacetamide used in this experiment was prepared according to the directions of Scholl.[1] Molecular proportions of chloroacetamide and the potassium salt of benzylsulfonamide were digested in absolute alcohol for about one hour, when the reaction was practically complete. Ammonia was always evolved during the digestion, indicating a partial hydrolysis of the amide. The alcohol was evaporated, when a dark colored residue was obtained, which dissolved in hot water. On cooling, the sulfonaminoacetamide separated in small, granular crystals. The compound was purified by crystallization from water or boiling 95% alcohol and melted at 157°. The amide is insoluble in absolute alcohol. It was dried for analysis over concentrated sulfuric acid.

Calc. for $C_9H_{12}O_3N_2S$: N, 12.30%, found, N, 12.08%.

Benzylsulfonaminoacetic Acid, $C_6H_5CH_2SO_2NHCH_2COOH$.—A quantitative yield of the sodium salt of this acid is obtained by digesting the above amide in sodium hydroxide solution until no more ammonia is evolved. After cooling the solution and acidifying with hydrochloric acid the sulfonglycocoll separates immediately on the form of plates. It crystallizes from boiling water or 95% alcohol in plates which melt at 149-150° to an oil. Schotten and Baumann's reaction was also applied with benzylsulfonchloride and glycocoll, but the yield of the acid was small and the greater portion of the acid chloride was converted into the potassium salt of the sulfonic acid.

Calc. for $C_9H_{11}O_4NS$: N, 6.13%; found, N, 6.01%.

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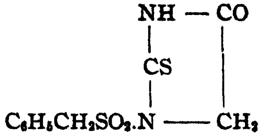
[1] *Ber.*, **29**, 2415.



2-Thio-3-benzylsulfonhydantoin .—Two grams of benzylsulfonglycocoll and 1 g. of dry ammonium thiocyanate were heated on the steam bath with 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid. After digesting for 20 minutes, the orange-colored solution was then poured into cold water, when the thiohydantoin separated as an oil, which finally solidified. This was purified by crystallization from boiling absolute alcohol and separated in yellow prisms, which decomposed at 204° with effervescence.

Calc. for $C_{10}H_{10}O_3N_2S_2$; N, 10.39%; found, N, 10.59%.

Benzylsulfonmethylaminoacetamide, $C_6H_5CH_2SO_2N(CH_3)CH_2CONH_2$. (*1*) *By alkylation of benzylsulfonaminoacetamide with methyl iodide.*—The potassium salt of benzylsulfonamide and the required amount of chloroacetamide were warmed in alcohol, as described above, in order to obtain the corresponding sulfonaminoacetamide. Without attempting to isolate the latter compound a molecular proportion of potassium hydroxide in absolute alcohol was added to the solution and finally an excess of methyl iodide. The mixture was then digested until neutral and the alcohol finally evaporated. We obtained a colored residue containing the above amide, which was dissolved in hot water. On cooling, the amide deposited in clusters of colorless crystals which melted at 206° to a clear oil. The amide is soluble in boiling alcohol and insoluble in cold water. It was dried for analysis at 100°.

Calc. for $C_{10}H_{14}O_3N_2S$: N, 11.59%; found, N, 11.46, 11.88, 11.80%.

(*2*) *By alkylation of methylbenzylsulfonamide with chloroacetamide.*—Benzylsulfonamide was first converted into its sodium or potassium salt and the latter then digested in alcohol with methyl iodide in order to obtain the correspondlng methylamide. When the reaction was complete, one molecular proportion of sodium ethylate in alcohol solution was added and finally the required proportion of chloroacetamide. There was an immediate reaction on warming and the solution was neutral to litmus and turmeric within 15–20 minutes. The alcohol was then evaporated under diminished pressure and the residue treated as in the first method. We obtained the amide melting at 206° to a clear oil. The yield was 25–30% of the theoretical, calculating from the amount of benzylsulfonamide used.

Benzylsulfonsarcosine, $C_6H_5CH_2SO_2N(CH_3)CH_2COOH$.—A quantitative yield of this acid was obtained by hydrolysis of the above amide with barium hydroxide. An aqueous solution of the amide and an excess of barium hydroxide was boiled until ammonia was no longer evolved. The barium was then quantitatively precipitated with sulfuric acid and the solution then concentrated by evaporation on the steam bath. On cooling, the acid separated in colorless prisms, which melted at 136° to an oil. The acid is soluble in hot water and alcohol.

Calc. for $C_{10}H_{13}O_4NS$: N, 5.78%; found, N, 5.65%

Hydrolysis of Benzylsulfonsarcosine with Hydrochloric Acid. The Formation of Sarcosine, $CH_3NH.CH_2COOH$.—This amide is slowly decomposed by boiling with concentrated hydrochloric acid. Sulfur dioxide is evolved and benzyl chloride distils with the aqueous vapor. The hydrolysis is effected easily by heating with hydrochloric acid at 120–130° in a pressure bottle. After heating for 2–4 hours the reaction was complete and benzyl chloride was suspended in the solution. The mixture was transferred to an evaporating dish and heated on the steam bath, when benzyl chloride volatilized with steam, leaving behind the hydrochloric acid salt of sarcosine. This was absolutely free from sulfur and dissolved easily in water. After decolorization with bone coal and concentrating the solution, sarcosine hydrochloride separated in colorless crystals. It was purified for analysis by recystallization from absolute alcohol and separated in colorless needles. The salt was dried for analysis by heating at 100°.

Calc for $C_3H_8O_2NCl$ N, 11.18%; found, N, 11.3%.

Benzyl-benzylsulfonamide, $C_6H_5CH_2SO_2NHCH_2C_6H_5$.—This amide was prepared by digesting, in alcohol, benzyl chloride with the potassium salt of benzylsulfonamide. It was purified for analysis by recrystallization from 95% alcohol and separated in colorless needles, on cooling, which melted at 145–146°. The amide is insoluble in hot and cold water and only slightly soluble in aqueous sodium hydroxide solution. The yield of the purified monobenzyl compound was 62% of the theoretical.

Calc. for $C_{14}H_{15}O_2NS$: N. 5.37%; found, N, 5.01, 5.25%

The Conversion of Benzyl-benzylsulfonamide into Benzylamine by Hydrolysis with Hydrochloric Acid, $C_6H_5CH_2NH_2$.—This amide was not changed by boiling with hydrochloric acid. On the other hand, when heated to 130° for 2.5–3 hours with hydrochloric acid, sulfur dioxide and benzyl chloride were formed, but only about one-fifth of the amide had been decomposed. Complete hydrolysis was effected by heating at 150° for 2–3 hours. After concentration of the solution the benzylamine hydrochloride was then identified by means of its double platinum salt. This was purified by crystallization from water and was dried for analysis at 100°.

Calc for $C_{14}H_{20}N_2PtCl_6$; Pt, 30.65%, found, Pt, 31.0%.

NEW HAVEN, CONN.

THE ACTION OF CHLORINE ON ETHYL CARBAMIC ESTER. THE ISOLATION OF ETHYLMONOCHLOROCARBAMIC ESTER AND ITS BEHAVIOR TOWARDS AMINES AND ACID AMIDES.

By Rasik Lal Datta and Satyaranjan Das Gupta

Received December 15, 1913.

The action of chlorine on carbamide and substituted carbamides was studied by Chattaway, who succeeded in preparing their various chloroderivatives. He prepared a dichloroderivative of carbamide by passing a current of chlorine through a well cooled, saturated solution of this compound.[1] Behal and Detauf[2] prepared monochlorocarbamide by passing a calculated amount of chlorine over carbamide and separating the monochlorocarbamide from carbamide hydrochloride, which is formed along with it, by cooling with methyl chloride. The other theoretically possible chloroderivatives have not as yet been prepared. Chattaway[3] tried the action of chlorine on alkyl and acyl substituted carbamides and was able to prepare the monochloro-, dichloro- and trichloroderivatives of the alkyl substituted carbamides and only the monochloroderivatives of the acyl substituted carbamides. The action of chlorine on phenylcarbamide[4] is interesting. In this case the chlorine atom not only takes the place of the hydrogen atom united to nitrogen, but also enters the phenyl radical; and he isolated, under different circumstances, no less than ten chloroderivatives from this body. The action of bromine on carbamide has been studied by one of us,[5] but it does not give rise to any bromoderivatives, though there are evidences of the latter being formed in solution.

The ready substitution of the hydrogen atoms, united to nitrogen atom of carbamide, by chlorine, with the production of unstable substituted nitrogen chlorides, suggested to us the possibility of replacing similar hydrogen atoms by chlorine in analogous bodies. The action of chlorine on ethyl carbamic ester is first taken into hand with a view to prepare its monochloro and dichloroderivative, since the formation of this is strengthened by the fact that it may be considered as carbamide in which one amido group is substituted by an alkylated hydroxyl. In fact, the monochloroderivative has been isolated as a pale yellow oil. The action of chlorine on ethyl carbamic ester was studied by Schmidt,[6] evidently with a view to isolate the monochlorocarbamic ester. But he failed to obtain the same and prepared instead a condensation product of urethane with dichloroacetaldehyde, *viz.*, dichloroethylidene-urethane, by allowing chlorine to act on the ester at a temperature ranging between 90–100°. The action that takes place, in this case, is quite different from what is expected for the formation of the chloroderivative. The urethane is first decomposed and the alkyl radical becomes simultaneously chlorinated and oxidized, forming dichloroacetaldehyde, thus:

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[1] *Proc. Roy. Soc.*, (*A*) 81, 381 (1908).

[2] *Compt rend.*, 53, 381 (1911).

[3] *J. Chem. Soc.*, 95, 129 (1909).

[4] Chattaway, *Ibid.*, 97, 292 (1910).

[5] Datta, *Ibid.*, 101, 166 (1912).

[6] *J. prakt. Chem.*, [2] 24, 120 (1881)

$$NH_2COOC_2H_5 + 3Cl_2 = CHCl_2.CHO + COCl_2 + NH_4Cl + HCl$$

which in turn further condenses with two molecules of the ester to form dichloroethylidene-urethane, thus:

$$CHCl_2CHO + 2NH_2COOC_2H_5 = CHCl_2.CH(NHCOOC_2H_5)_2 + H_2O.$$

Now, it has been found that if, instead of chlorinating the substance at the high temperature employed by Schmidt, the substance be chlorinated in well cooled aqueous solution, the monochlorocarbamic ester could be isolated very easily as a pale yellow oil. The preliminary experiment for the chlorination was carried out with a perfectly saturated and well cooled solution of urethane, with the view that the chloroderivative might be precipitated, similarly to dichlorocarbamide, by passing a current of chlorine through a saturated solution of carbamide. But, contrary to expectation, no such precipitate came out even after passing the current of chlorine for a good length of time, though the solution showed signs of considerable absorption of it. The only change that was noticeable was that the solution assumed a yellow color. This fact might account for the inability of Schmidt, who studied the action of chlorine on ethyl carbamic ester as pointed out before, to isolate the real compound.

Now, on pouring the resulting yellow solution into water, a pale yellow oil, which showed quite active properties, separated and sank to the bottom. Its action on potassium iodide resulted in the liberation of iodine, and it acts as a vigorous chlorinating agent. It was suspected to be the monochloroderivative of the ester and that was found to be the case.

The chloro compound is most conveniently prepared thus: A dilute aqueous solution of ethyl carbamic ester is taken and a current of chlorine is passed into it, when, within a very short time, a pale yellow oil separates at the bottom. The passing of chlorine is continued till the oil ceases to absorb it, that is, until no further deepening of the yellow color of the oil takes place. It has to be noticed that the oil separates from solutions which are dilute, while from saturated solutions no separation takes place until water is added to it. It is for this reason that a dilute solution and not a saturated one has to be employed. The oil is next separated by means of a separating funnel, washed with water and dried, when it is obtained as a pale yellow oil. If the oil be analyzed by separating it directly without washing, the percentage of chlorine comes out a trifle high, which is due to some chlorine dissolved in the oil. Like the nitrogen halogen derivatives, the chlorine in this is estimated by adding the oil to excess of potassium iodide solution and titrating the iodine liberated with sodium thiosulfate. Also a gravimetric halogen estimation was made according to Carius' method.

0.2535 g. liberated I = 20.3 cc. $N/10$ I; Cl as: NCl = 28 43%; 0.4163 g gave 0.04773 AgCl; Cl = 28.3%; calc. for $C_3H_6O_2NCl$: Cl = 28.74%.

The action that takes place is one of substitution, involving the liberation of one molecule of hydrochloric acid for each molecule of the ester chlorinated.

$$NH_2COOC_2H_5Cl = NHCl.COOC_2H_5 + HCl.$$

Since urethane is not a base, the liberated hydrochloric acid does not interfere with the chlorination of this substance and hence the compound is produced quantitatively, whereas in the case of the chlorination of dichlorocarbamide the liberated hydrochloric acid holds bound two-thirds of the urea employed as urea hydrochloride, and nearly one-third of the theoretical yield is obtained as pointed out before by one of us.[1]

The compound is a pale yellow, moderately viscous oil, having a refractive index of 1.44235 at 30°. It is tolerably stable, and during the chlorination no appreciable amount of hydrolysis takes place. The substance decomposes very slowly when kept in stoppered bottles; when kept in contact with water for some days, it yields a white crystalline substance which is under examination. The compound boils at about 90°, giving out bubbles of gas, evidently due to the decomposition of the compound. If the oil be heated to 140° and then allowed to cool, a solid substance begins to separate from the liquid and the stem of the tube is filled with a white, solid substance in the form of a sublimate. If it be heated in a bulb tube, a sudden rush of white vapors come out of the tube, which deposit on the upper part of the tube. On further heating, the whole thing chars, leaving a deposit of carbon. The composition of the solid which separates from the heated oil is also under investigation. The substance has a pungent smell, similar to chlorocarbamides. It has a remarkably corrosive and painful action on the skin; when applied to the skin a very painful sensation is felt in the course of a few minutes, which increases, gradually turning the skin violet-black. If the action be prolonged for some time, very painful and deep-seated scars are formed.

The compound is an extremely energetic agent, like dichlorocarbamide. But it has a great advantage over the latter, which has a great tendency of being hydrolyzed in the process of chlorination; this compound, however, effects chlorination smoothly and without the least amount of hydrolysis. For instance, in the chlorination of the lower aliphatic amines there is a vigorous hydrolysis with dichlorocarbamide; whereas the reaction takes place very smoothly and without the least hydrolysis with this body. So the reagent promises to be of signal service in cases of chlorination where free chlorine in not suitable, and where hypochlorous acid or dichlorocarbamide is too vigorous an agent effecting rapid hydrolysis. The chlorination of benzylamine was studied in detail as representing the amines, and that of benzamide, as representing the acid amides. It was also found that acetone interacts vigorously with it, forming a chloro compound. Its action on such bases as piperazine and hexamethylenetetramine is very interesting, and instead of chloroderivatives other condensation products, containing no halogen, are formed. These will be described in a future communication.

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[1] Datta, *J. Chem. Soc.*, **101**, 166 (1912).

The Action of Ethylchlorocarbamic Ester on Benzylamine.—The chlorination of benzylamine was effected by means of dichlorourea by one of us,[1] producing both monochloro- and dichlorobenzylamines. It has now been found that, by the action of the chloroester, both monochloro- and dichlorobenzylamines could be prepared according as the one or the other be employed in excess. For preparing monochlorobenzylamine, the chlorourethane is added to excess of benzylamine and the resulting product is treated with water, when the excess of amine dissolves in it, leaving monochlorobenzylamine as a pale yellow viscous oil. It was separated and dried as usual. Its identity was established by a halogen estimation.

0.2531 gave 0.2539 AgCl; Cl = 24.80%; calc for $C_6H_5CH_2NHCl$ Cl = 25.08%

The dichloro compound is prepared very easily by adding excess of ethylchlorocarbamic ester to benzylamine and then washing with water the pale yellow oil which separates. A halogen estimation in the dried substance proved the identity of the compound.

0.2160 gave 0.3505 AgCl; Cl = 40.15%; calc for $C_6H_5CH_2NCl_2$. Cl = 40.34.

The Action of Ethylchlorocarbamic Ester on Benzamide.—Benzamide could hitherto be chlorinated by means of sodium hypochlorite.[2] It has been recently shown[3] that chlorination in aqueous suspension is possible for the production of the monochloroderivative. The present chlorination by the chlorocarbamic ester is an addition to the methods of chlorination of benzamide. The chlorination of benzamide is effected most conveniently thus: Ethylchlorocarbamic ester is added to finely powdered benzamide with a small quantity of water. After allowing the reaction mixture to stand for some time, the chlorination becomes complete and the product is washed with water and recrystallized therefrom. Its melting point was found to be 116°, which is evidently of pure benzoylchloroamide.

The action of bromine on urethane in conjunction with soda was studied by Hantzsch,[1] and he obtained the dibromoderivative, four molecules of which are united chemically with a molecule of sodium bromide to form ethylic dibromoamidocarboxylate sodium bromide, $4NBr_2COOC_2H_5$, NaBr, as a yellow granular powder the sodium bromide of which is firmly in union and cannot be removed by washing with water. It is most likely that the constitution of this body is quite different from what has been assigned to it by Hantzsch. In all probability it has a complicated formula, as can be inferred from the unstable nature of the monochlorocarbamic ester as also from the less energy of bromine for reactions of this kind. It might be a condensed compound having the formula given below:

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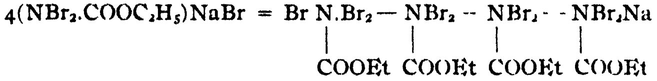
[1] Datta, THIS JOURNAL, 34, 1613 (1912).

[2] Bender, *Ber.*, 15, 410 (1882).

[3] Datta and Ghosh, THIS JOURNAL, 35, 1044 (1913).



$$4(NBr_2.COOC_2H_5)NaBr = Br\,\underset{\substack{|\\COOEt}}{N.Br_2} - \underset{\substack{|\\COOEt}}{NBr_2} - \underset{\substack{|\\COOEt}}{NBr_2} - \underset{\substack{|\\COOEt}}{NBr_2Na}$$

The formation of such a compound may be explained thus: Bromine acting on urethane in conjunction with soda forms NaBrNCOOEt, analogous to the formation of potassium acetobromoamide by the action of bromine and caustic potash on acetamide. Now this further adds two atoms of bromine to form $NBr_3NaCOOEt$, making the nitrogen pentavalent. Four molecules of this condense, with the elimination of sodium bromide, to form the above compound.

$$4NBr_3NaCOOEt = 3NaBr + 4NBr_2COOEt, NaBr.$$

We are at present engaged in preparing the chloroderivatives of other esters of chlorocarbamic acid and also of alkyl and acyl substituted carbamic esters.

We take this opportunity of expressing our best thanks to Prof. P. C. Ray for the interest he has taken in the above investigation.

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ACYL DERIVATIVES OF o-AMINOPHENOL.

By J. H. Ransom and R. E. Nelson

Received December 1, 1913.

In an extended piece of work published some years ago the senior author[2] found that when *o*-nitrophenylethylcarbonate is reduced with tin and hydrochloric acid a urethane is obtained soluble in bases and evidently having the carbethoxy radical attached to nitrogen. By modifying the conditions, a basic substance was isolated in which the carbethoxy radical is attached to oxygen. On standing, this rapidly changes to the urethane. The same urethane was obtained from *o*-aminophenol and chlorocarbonic-ethylether in ether solution. A similar rearrangement occurs when *o*-nitrophenylbenzoate is reduced in acid solution. In determining the constitution of the urethane, Ransom made the diacyl derivative, using benzoyl chloride in alkaline solution. He found that the same diacyl derivative is produced when benzoyl *o*-aminophenol is treated with chlorocarbonic-ethylether. In both cases saponification gives benzoic acid and hydroxyphenylurethane, indicating that in the latter case a molecular rearrangement has occurred, so as to leave the lighter acyl group attached to nitrogen. Other diacyl derivatives were made and in every case the lighter acyl group was found attached to nitrogen. But if one of the amine hydrogen atoms is first replaced by a hydrocarbon radical no rearrangement occurs, isomeric substances being formed when the acyl radicals are introduced in reverse order. The same is true when the amine and hydroxyl groups are in the meta or para position to each other.

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[1] *Ber*, 27, 1248 (1894).

[2] *Am. Chem. J.*, 23, 1.

It seemed desirable to determine if a carboxylester group would become attached to nitrogen in place of a lighter carbonyl group already there; also, if of two carboxylester groups introduced the lighter one would go to the nitrogen. Finally it seemed of interest to determine if rearrangement would occur in case the radicals introduced were of nearly the same weight. If the rearrangement did not occur, or proceeded more slowly, it was thought there would be a better chance of studying the mechanism of the rearrangement.

Hydroxyphenylisoamylurethane.—Two grams of *o*-aminophenol were suspended in ether and the calculated amount (2 mol.) of chlorocarbonic-isoamylether slowly added. The hydrochloride of one molecule of the *o*-aminophenol precipitated. After filtering, the ether solution was evaporated, leaving about two grams of a solid. It crystallized from boiling ligroin in white needles melting at 68.5–69.5°. The crystals are insoluble in cold water and dilute acids, but are sparingly soluble in hot water, and very soluble in chloroform, benzol, alcohol and ether. The compound is also quite soluble in dilute alkalies from which solution it is precipitated by acids, showing its acid character.

The same substance was also made by the reduction, with tin and hydrochloric acid, of *o*-nitro-isoamylcarbonate (made according to Ransom's method). The melting point was the same and a mixture of the two had the same melting point as either.

Another quantity of *o*-nitro-isoamylcarbonate was reduced, but as soon as the action was complete the product was thrown into a concentrated solution (1 : 1) of potassium hydroxide kept cold in a freezing mixture. This solution was quickly extracted with ether and the ether solution dried with potassium hydroxide. When dry, the ether was saturated with dry hydrochloric acid. A white precipitate separated which was filtered out and quickly dried on a porous plate in a desiccator. The melting point was 134° and the substance was quite soluble in cold water and acids;

but alkalies precipitated an oil from the solution. A small amount was dissolved in water and allowed to stand. Soon an oil separated which was extracted with ether and the ether evaporated. A solid remained which was soluble in alkalies and had all the properties of the urethane described above. Evidently the substance melting at 134° is the hydrochloride of *o*-aminophenyl-isoamylcarbonate which changes to the urethane on being warmed with water. In the dry condition it is quite stable.

Benzoylhydroxyphenylisoamylurethane.—1.5 grams of the hydroxyphenylisoamylurethane were dissolved in potassium hydroxide solution and to this was added 0.8 gram of benzoyl chloride. Slowly a brown oil separated which solidified with difficulty in the cold. After recrystallizing several times from dilute alcohol white needle-shaped crystals were obtained, melting at 65.5°. The substance is insoluble in water, dilute acids and alkalies; but soluble in ether, chloroform, benzol and alcohol. 0.2591 g. gave 10 cc. of nitrogen at 22.5° and 748 mm. pressure. This is equivalent to 4.39% of nitrogen. Calculated for $C_{19}H_{21}NO_4$ the nitrogen equals 4.28%. Saponification of the substance with alcoholic potash produced benzoic acid and the urethane melting at 68.5-69.5°. A mixture of the two had the same melting point.

Action of Chlorocarbonic-isoamylether on Benzoylaminophenol.—Benzoyl *o*-aminophenol was prepared by Ransom's method and 2 grams of it, in alkaline solution, were treated with 1.6 grams of chlorocarbonic-isoamylether. An oil separated which was extracted with ether and the ether evaporated. Recrystallized from dilute alcohol the substance formed white crystals melting at 65.5° and its mixture with the supposed isomer had the same melting point. Saponification, as above, gave the same substances. Evidently the benzoyl group, in this as in the former case, is attached to oxygen and must have shifted from its original attachment to nitrogen.

Action of Chlorocarbonic-isoamylether on Hydroxyphenylethylurethane.—The ethyl urethane was prepared as stated and 2 grams of it, in alkaline solution were treated with the calculated amount of chlorocarbonic-isoamylether. A light yellow oil separated which was extracted with ether. On evaporating the ether an oil was left which did not solidify until it was distilled *in vacuo*. After several recrystallizations of the distillate from alcohol the white crystals melted at 65-66°. On saponifying some of the impure material two substances were obtained. A small part melted at 133–134° and is probably carbonylaminophenol, produced from the urethane by loss of alcohol. The other part melted at 84–85° and on being mixed with hydroxyphenylurethane (m. p. 86–87°) the melting point was raised slightly.

Action of Chlorocarbonic Ethylether on Hydroxyphenylisoamylurethane.—1.4

grams of the isoamylurethane were treated, in alkaline solution, with 0.7 gram of chlorocarbonic ethyl ether. A heavy red oil separated which would not solidify until it was distilled *in vacuo* (185-200° at 15 mm. pressure). After several recrystallizations of the distillate the crystals became white and melted at 65-66°. They are insoluble in acids and alkalies, but quite soluble in alcohol, ether, chloroform and benzol. Mixed with the possible isomer, described above, the melting point was not depressed. Evidently in this case a molecular rearrangement occurs as expressed in the following equation:

$$KOC_6H_4NHCOOC_5H_{11} + ClCOOC_2H_5 \longrightarrow KCl +$$
$$C_2H_5OOCOC_6H_4NHCOOC_5H_{11} \longrightarrow C_5H_{11}OOCOC_6H_4NHCOOC_2H_5.$$

The final product is carbamyl *o*-hydroxyphenylethylurethane.

Summary.—The work here outlined, together with that previously reported, shows that when two carboxyl radicals ($COOR$ and $COOR_1$) are introduced into the molecule of *o*-aminophenol the lighter one becomes attached to nitrogen, the position not being influenced by the order in which the groups are introduced; and that to accomplish this, a molecular rearrangement occurs in one case. This is also true when both of the radicals are carbonyls (COR and COR_1). In case one radical is carbonyl and the other carboxyl the latter becomes attached to nitrogen without being influenced by the relative weights of the entering groups. The hope that the introduction of radicals of nearly the same weight (C_6H_5CO and $C_5H_{11}COO$) would result in the formation of isomeric substances was not realized, the velocity of the rearrangement being, apparently, almost instantaneous in every case. Consequently the mechanism of the rearrangement is still in doubt. It is possible that there is equilibrium of the two isomeric forms, one always being in too small amounts to be isolated, but there is little evidence to support this view. Work already begun with the orthoaminomercaptans may still throw light upon the problem.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORIES. NO. 227]

A STUDY OF THE CHEMICAL CONSTITUTION OF INVERTASE.

[FIRST PAPER.]

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Since enzymes play such important roles in most chemical reactions occurring in plants and animals, any knowledge as to their true chemical constitution is of obvious importance. In a study of this kind it is desirable to select an enzyme which can be had in comparatively large amounts and can be easily purified. Such an enzyme is yeast invertase. Pressed yeast can be obtained from breweries and the invertase can be isolated by autolytic or extraction methods.

The constitution of invertase has already received considerable attention. In this connection may be mentioned the work of O'Sullivan and Tompson[1] who were probably the first to come to any important conclusions. Their results indicate invertase to be a water soluble substance made up of a carbohydrate and an "albuminoid" or protein. The latter seemed identical with the protein obtained from yeast itself. Another investigator, Salkowski[2] regarded the polysaccharide in invertase as an impurity which he called "yeast gum." He doubted the protein character of the nitrogenous part, because of its weak response to the Millon, xanthoproteic and biuret tests. Wroblewski[3] came to similar conclusions regarding the carbohydrate part, but differed with Salkowski in believing invertase to contain a very active protein, which he claimed he succeeded in isolating by salting out with ammonium sulfate. Osborne[4] prepared invertase which had a nitrogen content of about 6.1% and which gave Millon, xanthoproteic and biuret tests. In spite of these tests and on the basis of its empirical composition he likens it to chitin. Hafner,[5] showed that invertase contained phosphorus in organic combination, a fact neglected by most investigators. He could not obtain the biuret test, and thought invertase was a complicated substance containing besides phosphorus, a carbohydrate and a nitrogenous group which he was unable to isolate. Euler and his students[6] have succeeded in preparing the most active invertase known thus far ($\pm 0^\circ$ = 10 to 20 minutes), and the nitrogen content of which varied from 1.85 to 4.59%. They suggest that invertase closely approaches yeast gum in its chemical constitution, but express no opinion as to the nature of the nitrogenous part. Mathews and Glenn[7] suggest that the active principle in invertase may be protein in character and conclude that the carbohydrate part serves as a colloidal ferment bearer for this active protein.

From the above it can be seen that, so far, very little has been definitely determined concerning the chemical constitution of invertase, except that all products prepared thus far contain a polysaccharide, a nitrogenous substance and phosphorus. The results obtained in this laboratory confirm in general the opinions of O'Sullivan and Tompson. More data was secured showing the nitrogenous part to be protein and the phosphorus to be chemically combined with the carbohydrate.

[1] *J. Chem. Soc.*, **57**, 834 (1890).

[2] *Z. physiol. Chem.*, **31**, 305 (1900).

[3] *J. prakt. Chem.*, **64**, 1 (1901); *Ber.*, **36**, 1134 (1898).

[4] *Z. physiol. Chem.*, **28**, 399 (1899).

[5] *Ibid.*, **42**, 1 (1904).

[6] *Ibid.*, **65**, 124 (1910); **69**, 152 (1910); **72**, 340 (1911); **73**, 335 (1911).

[7] *J. Biol. Chem.*, **9**, 29 (1911).

Preparation of Invertase.—Two hundred pounds of pressed yeast were placed in a barrel, some toluene added to prevent bacterial growth, and the yeast allowed to autolyze, at room temperature, from two to six weeks. At first, a strong fermentation, with the evolution of large amounts of carbon dioxide, took place and later liquefaction. Several types of filter presses and centrifuges were tried for filtering the large amount of liquid, but these were found to be unsuccessful and finally large folded papers with parchmentized tips were used. In this way five to six gallons of a clear yellow liquid were obtained to which was added an equal volume of 95% alcohol. A flocculent yellow precipitate settled out, the alcohol was decanted and the residue dissolved in water. There was left a considerable amount of insoluble matter, probably consisting chiefly of insoluble proteins. To this aqueous extract, alcohol was added. This time the precipitate was gummy instead of flocculent and, after decanting the alcohol, it dissolved almost completely in water, giving an opalescent solution which was filtered when necessary. A concentrated solution of lead acetate was then added with stirring, until practically no more precipitate formed, care being taken to avoid an excess of the reagent. After filtering off the lead precipitate, potassium oxalate was added to throw down the lead remaining in the solution, and after filtering, the filtrate was treated with kaolin and stirred constantly for an hour. The kaolin treatment was generally repeated two or three times. The resulting liquid was placed in collodion bags, containing some toluene, and dialyzed in running water from three to twenty days. After dialysis, the invertase, as O'Sullivan and Tompson pointed out, could no longer be precipitated by the addition of several volumes of alcohol alone, and it was necessary to add also some electrolyte to destroy the colloidal solution. For this purpose a small amount of sodium chloride, potassium acetate or acetic acid was found satisfactory. A mechanical stirrer was found useful in hastening the coagulation of the precipitate at this point. The gummy precipitate was ground in a mortar with absolute alcohol, whereupon the precipitate gradually changed into a white powder which was easily filtered on a suction filter and finally washed with absolute alcohol and ether. This product was then dried in a vacuum over sulfuric acid for several days. From two hundred pounds of yeast about two hundred grams of invertase were obtained.[1]

The above method of isolation and purification was adopted since it corresponded more closely with those used by such other investigators as O'Sullivan and Tompson, Euler, and Mathews and Glenn, both in procedure and composition of the preparations. It really amounts to a purification of the yeast gum or carbohydrate part, and experiments are being conducted now, in this laboratory, to see whether it is advisable, or not, to change this form of procedure.

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[1] The authors wish to thank Messrs C W. Otto and L. Siegler for their valuable assistance in some of the experimental work.

Properties of Invertase.—The invertase obtained by the above method was a white powder, soluble in water, and giving a slightly opalescent solution. It gave the biuret, Millon and xanthoproteic reactions for proteins, when sufficient material was used. Mathews and Glenn had great difficulty in obtaining the biuret test, and Hafner could not obtain it at all. These reactions are important in view of the fact that the preparations were as low in nitrogen content as that of any other investigator and the activity ($\pm 0° = 37$ minutes at 37°) was comparable with that of O'Sullivan and Tompson, and Mathews and Glenn.

The water solution gave no precipitate with phosphotungstic acid, mercuric acetate, nor lead acetate, and could not be salted out by ammonium, magnesium or zinc sulfates. It did not coagulate on heating. The average preparations had a nitrogen content of 1.3%; ash, 0.9%; and phosphorus, 0.3%.

Analysis of the Invertase Preparations.—The samples were dried at 70° to constant weight. The ash values were obtained with a special ashing burner at low red heat; the phosphorus was obtained by sodium carbonate and potassium nitrate fusion, dissolving in nitric acid, precipitating first with molybdate and finally with magnesia mixture and weighing as magnesium pyrophosphate; the nitrogen was determined by the ordinary Dumas method.

Activity of the Invertase Preparations.—This was determined according to the method of O'Sullivan and Tompson, subsequently used by Euler and his co-workers.[1] The principle underlying this method is the determination of the length of time required by a given amount of invertase to perform a definite amount of work, under standard conditions of temperature, concentrations of cane sugar, invertase and hydrogen ion. This amount of work is expressed as the time in minutes in which a definite amount of invertase reduces the rotation of 100 times its weight of cane sugar to ±0°.

All determinations were carried out in a constant temperature water bath at 37°, and not varying more than ±0.01° and in an optimum hydrogen ion concentration. The rotation was read in a water-jacketed polariscope tube, kept accurately at 35°, and similar to the one used by Hudson.[2] The following determination is given in order to illustrate the method: Fifty milligrams of an invertase preparation were dissolved in 5 cc. of $N/2$ acid sodium phosphate solution and added to 20 cc. of a cane sugar solution, containing 4 grams of the sugar, both solutions being previously warmed to 37° C. At the end of half an hour the inversion was stopped by the addition of 5 cc. of a strong sodium carbonate solution. Rotation of the solution without inversion (Blank) in a 220 mm. tube, temperature 35° and sodium light, was +18.97°, and after inversion +1.25°. Calculating, by means of $\alpha^{35°}_{D}$ (specific) rotation for cane sugar and invert sugar, the amount of inversion, and then applying the method given by O'Sullivan and Tompson, the activity was found to be ±0° = 37 minutes at 37°.

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[1] *Z. physiol. Chem.*, **69**, 152 (1910).

[2] THIS JOURNAL, **30**, 1564 (1908).

The following analytical results were obtained for 9 samples:

No of sample	Period of dialysis Days	Ash. Per cent.	Nitrogen Per cent.	Phosphorus Per cent.	Activity at 37° ± 0[1] Minutes
1	0	5.25	2.21	.	37
2	3	1.30	1.51	0.27	154
3	3	0.85	1.61	0.27	72
4	7	0.80	1.26	0.26	37
5	7	1.02	1.28	0.27	52
6	10	0.89	1.35	0.27	136
7	14	0.88	1.83	0.29	70
8		1.49	1.35	0.32	953
9		1.68	1.36	0.30	none

The Chemical Constitution of the Polysaccharide of Invertase.

Schützenberger[2] was the first to isolate yeast gum from yeast by extraction with water and precipitation with alcohol. Hessenland[3] showed that it gave mannose and glucose on hydrolysis. Salkowski[4] prepared it by precipitation from yeast extract with Fehling's solution. Meigen and Spreng[5] found Salkowski's method for isolating the gum the best, and by hydrolysis obtained twice as much mannose as glucose. Euler and Fodor[6] showed this gum was present in invertase preparations, a fact previously shown by Salkowski and Wroblewski,[7] and by hydrolysis found its composition to be between 4 mannose, 3 glucose and 4 mannose and 4 glucose. In the present investigation, the behavior of the gum towards acetolysis has been studied, also the phosphorus content of the acetylated products and the gum itself has been determined.

Preparation of the Yeast Gum.—The yeast gum was prepared from invertase by Salkowski's method.

Twenty grams of invertase were dissolved in 150 cc. of 3% potassium hydroxide solution, and warmed on the water bath for half an hour. About 200 cc. of Fehling's solution were then added, the copper gum precipitated and collected in a spongy mass. The excess of Fehling's solution was decanted and the gum washed with water to remove the excess alkali. It was then placed in a mortar, ground up with water and a few drops of concentrated hydrochloric acid, until all had gone into solution. The gum was reprecipitated from this solution by means of alcohol, redissolved in distilled water, and again precipitated by means of alcohol. This last treatment was repeated three times, the gum then put in absolute alcohol, and after it had crumbled to a fine, white powder, was washed with ether and dried in a vacuum over concentrated sulfuric acid. The gum left no ash on ignition, was free from copper and nitrogen, but contained phosphorus, a fact which seems to have been overlooked by most investigators. Phosphorus was determined in the same way as in invertase itself. One sample showed 0.32% phosphorus while another not quite so pure showed 0.23%.

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[1] The degree of activity was not relied upon as a criterion of purity, as many investigators have done heretofore, since this property, besides being dependent upon the composition, is also influenced by the way it is precipitated with alcohol, and very likely many other conditions at the present little understood.

[2] *Bulletin*, [2] **21**, 204 (1874).

[3] *Z. Ver. Rübenzuckerind.*, **42**, 671 (1892).

[4] *Z. physiol. Chem.*, **31**, 305 (1900).

[5] *Ibid.*, **55**, 48 (1908).

[6] *Ibid.*, **72**, 340 (1911).

[7] *J. prakt. Chem.*, **64**, 1 (1901).

To determine whether any of the phosphorus of the original invertase had been split off by the Fehling solution, the Fehling filtrate from the gum was acidified with hydrochloric acid, treated with hydrogen sulfide to remove copper, filtered, evaporated to dryness, and tested for phosphorus A very slight amount of molybdate precipitate was obtained, but it was so small that magnesia precipitation gave negative results. From these results it seems probable that all the phosphorus is chemically combined with the gum.

Action of Acetyl Bromide on Invertase.—Two grams of invertase, dried *in vacuo* at 55°, were treated with 10 cc. of acetyl bromide in a flask provided with a ground in reflux condenser surmounted by a calcium chloride tube. At first the reaction was rapid with evolution of hydrobromic acid but as it diminished in speed, it seemed best to heat gently on the water bath. Most of it went into solution rapidly, but a small amount required longer treatment. On account of the small amount of the latter, no attempt was made to isolate and to see whether it was different from the rest. After all had dissolved, the brown syrup was poured into ether (ethereal solution, see below), whereupon a yellowish white precipitate settled out. The precipitate was soluble in hot alcohol, and on cooling settled out in what seemed to be microscopic crystals but which, on further examination, were found to be amorphous.[1] This product was reprecipitated from alcohol four or five times. The substance did not reduce Fehling's solution, but gave a white precipitate. It was soluble in acetone, ethyl acetate, and hot alcohol, insoluble in ether. It began to soften at 178° and melted with decomposition at 198°. The substance contained phosphorus. The yield was about 1.5 grams. Upon analysis two samples gave, respectively, the following results:

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[1] In one or two instances we have noticed needles one or two mm. in length adhering to the stirring rod in the beaker.

C = 49.44, 49.03%; H = 6.27, 6.39%; P = 0.31, 0.29%; Acetyl value = 44.44%.

The acetyl values were obtained by dissolving a weighed amount in 50 cc. of methyl alcohol; 50 cc. of *N*/10 sodium hydroxide were then added, allowing the solution to stand over night and titrating with *N*/10 acid in the morning.

The ethereal solution, mentioned above, was washed with ice-cold sodium bisulfite solution, with ice water, with sodium carbonate solution, and again with ice water. It was then dried over calcium chloride and evaporated *in vacuo*. It left a very small amount of a brown syrup, insoluble in ligroin, and soluble in alcohol. So far, no crystals have been obtained from the syrup.

Action of Acetyl Chloride on Invertase.—Invertase was also treated with acetyl chloride, but even at boiling temperature there was very little action. This was to be expected from the behavior of acetyl halides on other carbohydrates.

Action of Acetic Anhydride and Sulfuric Acid on Invertase.—Five grams of invertase, dried *in vacuo* at 55°, were heated on a water bath with 50 cc. of acetic anhydride, to which 0.5 cc. of concentrated sulfuric acid had been previously added. In a short time, the mixture dissolved completely with slight darkening. The crude acetyl derivative was precipitated in light yellow flocks by pouring it into a mixture of one part gasoline and four parts of ether. These were redissolved in hot alcohol, boneblacked, filtered and allowed to cool, when the acetyl derivative usually separated as a snow white amorphous solid; but in one or two instances, we noticed needles 1 or 2 millimeters long adhering to the stirring rod in the beaker. It was very hydroscopic, soluble in acetone, ethyl acetate, hot alcohol. chloroform, slightly soluble in cold alcohol, insoluble in ligroin, gasoline, and ether. It melted with decomposition at 184–198°.

Analysis of two samples gave the following results, respectively:

Acetyl value = 42.5, 42.5%; P = 0.25, 0.28%; no N.[1]

To investigate the nature of the monosaccharides occurring in this acetyl derivative, two grams of the above acetyl derivative were hydrolyzed for 12 hours with 300 cc. of 5% sulfuric acid, neutralized with barium hydroxide, the excess of barium removed with CO_2, filtered, evaporated to small bulk, cooled, phenylhydrazine acetate added, allowed to stand 24 hours in cold, filtered on weighed Gooch, and the crystals washed with cold water. Two grams of acetyl invertase gave 0.8612 gram mannose hydrazone = 0.5741 gram mannose = 28.7% mannose. The filtrate, after heating on the water bath, gave a test for glucosazone. Time did not permit direct determination of glucose content, or testing for other monosaccharides.

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[1] Of the many samples of this acetyl derivative examined, all values for phosphorus were between these two values except one which was 0.73%. As there seemed no error in the determination this result is given.

The above series of experiments show that not only the polysaccharide in invertase contains phosphorus, but also the acetylated compounds derived therefrom.

This very interesting fact, that the phosphorus is combined with a polysaccharide, brings out another class of naturally occurring compounds, the phosphorized polysaccharides. Ford has stated[1] that it is very difficult to obtain starch free from phosphorus, and Kiliani[2] has noted the same fact about inulin. Perhaps these substances in their naturally occurring state are also partially phosphorized polysaccharides. While the acetylated polysaccharide contains almost the same per cent. of phosphorus as the original gum by allowing for the 44% acetyl, the phosphorus content of the polysaccharide itself has been almost doubled, showing that part of the polysaccharide has been split off by the acetolysis, and it is probably this part that goes into the ether solution.

The Chemical Constitution of the Nitrogenous Constituents.

O'Sullivan and Tompson fractionally separated their invertase into a series of seven substances which they called "invertans." The first member contained 8.35% nitrogen but was low in carbohydrates, while the last member contained only 1.05% nitrogen and had a high carbohydrate content. From the member high in nitrogen they isolated a nitrogenous substance, after removing the carbohydrates by precipitation with alkaline copper solution, and found it to be a protein (nitrogen 14%) identical with the protein in yeast itself. Furthermore, they concluded that the invertans consisted of various amounts of carbohydrates and this protein.

Wroblewski, as previously stated, claims to have salted out a very active protein from a Merck's preparation of invertase by means of ammonium sulfate. He gives no analysis, but seems to rely on biuret and Millon tests as an evidence for its being a protein. In this laboratory, it has been found impossible to salt out the protein in this manner. Nearly all the other investigators were unsuccessful in isolating any substance which, upon analysis, had a sufficiently high nitrogen value to be a protein. Moreover many were led to doubt the protein character of this constituent because of the weak biuret, Millon, and xanthoproteic tests.

Hafner[3] attempted, but failed, to isolate the nitrogenous constituent by hydrolysis of invertase with $2^1/_2$% sulfuric acid, and subsequent precipitation of the nitrogenous substance with phosphotungstic acid.

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[1] *J. Soc. Chem. Ind.*, **23**, 414 (1904).

[2] *Ann.*, **205**, 147 (1888).

[3] *Z. physiol. Chem.*, **42**, 1 (1904).

It was found that, before hydrolysis, a 10% solution of invertase was not precipitated by any of the ordinary protein precipitants, while after hydrolysis with sulfuric acid and neutralization with barium carbonate, copious precipitates were obtained with phospho-molybdic acid, phosphotungstic acid, mercuric acetate, and mercuric chloride. This indicates that in the original invertase the nitrogenous or protein part is either combined with the carbohydrate or the latter acts as a protective colloid. In either event, the properties of the protein are effectually masked in the invertase.

The following series of experiments was made to determine the concentration of sulfuric acid to be used and the time necessary for this hydrolysis, in isolating the nitrogenous substance: Five grams of invertase were placed in each of four Erlenmeyer flasks with 50 cc. of 20, 10, 5 and $2^1/_2$% sulfuric acid, respectively, and immersed in a water bath kept at 100° C. At two-hour intervals, two samples of five cc. each were pipetted from each flask, and cooled to room temperature. To one, 5 cc. of a 10% solution of phosphotungstic acid were added, the other was neutralized with sodium hydroxide and then added to an equal volume of Fehling's solution.

H_2SO_4	Precipitate with phosphotungstic				Precipitate with Fehling's solution			
Per cent.	2 hrs	4 hrs	6 hrs	8 hrs	2 hrs	4 hrs	6 hrs	8 hrs
20	heavy	heavy	heavy brown	very brown	none	none	none	none
10	heavy	heavy	heavy yellow	heavy brown	none	none	none	none
5	slight	moderate	heavy	heavy	heavy	moderate	none	none
$2^1/_2$	very slight	slight	moderate	moderate	heavy	moderate	moderate	moderate

The above results show that four hours' hydrolysis with a 10% sulfuric acid gives the best results.

Twenty grams of invertase were hydrolyzed four hours with 200 cc. of 10% sulfuric acid at 100°. The solution was then filtered from a slight amount of insoluble matter, cooled, and phosphotungstic acid added until no more precipitate collected, the precipitate was filtered, and washed with 10% sulfuric acid. The precipitate was then boiled for an hour or so with an excess of barium hydroxide solution, the precipitate of barium sulfate and barium phosphotungstate filtered off, the filtrate saturated with CO_2 to remove barium, solution filtered, evaporated to small bulk (5 cc.), filtered from a slight amount of barium phosphotungstate, and then added to three volumes of absolute alcohol; a flocculent precipitate settled out. This substance was quickly filtered on a platinum Gooch, washed with absolute alcohol and ether and weighed. Yield, about 0.25 gram. The yield was not always as satisfactory. This was due to the difficulties involved in the method, and also to the fact that a quantity of the protein itself was probably hydrolyzed in the preliminary treatment. This protein was soluble in water, not coagulated either by heating or hydrochloric acid, was precipitated by phosphotungstic acid, and gave a very strong biuret reaction. It gave no test for phosphorous after digestion with nitric acid, etc., and no reduction or precipitate with Fehling's solution. It is extremely hydroscopic.

0.0534 gram gave 6.6 cc. N at 25° and 757 mm. = 13.7% N.

Another sample from a different invertase gave:

0.0063 gram gave 0.6 cc. N at 26° and 765 mm. = 10 7% N

Due to the small amount of sample the latter value is not as trustworthy as the former.

In another experiment 20 grams of invertase were hydrolyzed for four hours with 10% sulfuric acid, the resulting solution neutralized with barium carbonate, filtered, evaporated to half bulk, mercuric acetate added instead of phosphotungstic acid, the flocculent precipitate filtered, washed, decomposed with hydrogen sulfide, solution filtered from the mercuric sulfide, evaporated to about 5 cc., and precipitated with absolute alcohol. A heavy flocculent precipitate was obtained which gave no reduction with Fehling's solution, and no test for phosphorus, but showed a strong biuret reaction. The yield was very poor.

Analysis:

0.0519 gram substance gave 4.8 cc. N at 26° and 757 mm. = 10 2% N

This result is probably low because it was impossible to separate all the barium carbonate from the protein.

Assuming all the nitrogen to be protein, only about 10% of it could be isolated by either the phosphotungstic acid or mercuric acetate methods. This is probably due to experimental difficulties. Still, it is impossible to say that all of the nitrogen in invertase is protein in character. Although a great number of experiments were made, testing the presence of purines, pyrimidines, and volatile bases, no evidence was obtained that any of the nitrogen was other than protein in character.

Salting out Experiments after Partial Hydrolysis.—After the hydrolysis with 10% sulfuric acid, and neutralization with ammonium hydroxide, small amounts of a gelatinous precipitate were obtained with ammonium sulfate, magnesium sulfate and zinc sulfate, although before hydrolysis these salts gave no precipitate. These precipitates, when filtered, gave strong biuret reactions. The filtrates, however, also gave good biuret reactions, showing that all the protein is not salted out by these reagents.

Twenty grams of invertase were hydrolyzed with 10% sulfuric acid under the same conditions as above, and were then placed in collodion bags and dialyzed for thirty-six hours in running water. At the end of that time, the contents of the bags were tested for protein, but gave negative results, showing that all the protein had dialyzed.

The Action of Enzymes on Invertase.—Wroblewski[1] showed that invertase was not destroyed by the action of trypsin, and Mathews and Glenn found that the gum was not digested by diastase. Similar results were obtained in this laboratory with ptyalin and pancreatic amylase. They were allowed to stand in contact with the gum from invertase over 12 hours, and at the end of that time no reduction with Fehling's solution could be noticed. Castor bean lipase also gave negative results.

The authors wish to take this opportunity to express their thanks and appreciation to the Jacob Ruppert Brewery, New York City, for furnishing such ample amounts of pressed yeast.

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THE PICRATE COLORIMETRIC METHOD FOR THE ESTIMATION OF CARBOHYDRATES.

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The quantitative estimation of sugars and other carbohydrates involves the use of the polarimeter or the oxidizing power of copper solutions; as yet no accurate application of colorimetric methods[2] has been made to carbohydrates.

The method herein described depends upon the formation of a red-to-brown color when solutions of sugars are heated with *sodium carbonate solutions of picric acid.* These colors were first described by Braun;[3] other observers were Jaffé,[4] Johnson[5] and Chapman.[6] All these investigators used caustic alkalies instead of sodium carbonate, hence the colors obtained resulted not only from the reduction of picric acid by the sugars, but also from the caramelization of sugars by the alkali.[1] This latter effect is entirely avoided in the use of sodium carbonate.

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[1] *J. prakt. Chem.*, 64, 1 (1901).

[2] Dubrunfaut devised a method for estimating glucose by comparing the color developed by treating sugar solutions with alkali. Heller (*Archiv.*, 1, 212; 4, 310; *Z. anal. Chem.*, 28, 650; *Deut med. Wochschr.*, 1888, 451) made modifications of this method. Neitzel (*Chem. Ztg.*, 1894, Rep. 93; *Z. Rübenzucker-ind.*, 1894, 221) used a modification of Molisch reagent (*Monatsh.*, 7, 198). Johnsoh (*Z. anal Chem.*, 23, 111; *Brit. Med. J.*, 1883, 504; *Pharm. J. Trans.*, 54, 24; *Deut. med. Wochschr.*, 1888, 451, 479; *Pharm. Prax.*, 1880, 1, 103) used picric acid and potassium hydroxide. Autenreith and workers (*Munch med. Wochsch.*, 57, 1780; 58, 899; 59, 689) oxidized by Bang's solution (*Biochem. Z.*, 2, 271; 32, 443) and estimated colorimetrically the unchanged copper. Järvinsen (*Z. anal. Chem.*, 52, 14) makes use of Almen-Nylander's reagent (*Ibid.*, 9, 494; *Z. physiol. Chem.*, 50, 36; *Biochem. Z.*, 16, 489). For other applications of colorimetry to carbohydrates see Neitzel, *Z Spiritusind.*, 20, 163; Ruini, *Gazz. chim. ital.*, 31, 445; Lyons, *Pharm. Rev.*, 20, 155; Dennstedt and Voigtländer, *Forschungsb. ü. Lebensmittel*, 2, 173; Ambuhl, *Chem. Ztg.*, 19, 1508.

[3] *Z. Anal. Chem.*, 4, 185; *Chem. Zentr.*, 1866, 219; 1874, 825; *J. prakt. Chem.*, 96, 412. Braun mentions that glucose, fructose and lactose give these colors

[4] *Z. physiol. Chem.*, 10, 391.

[5] *Pharm. J. and Trans.*, 54, 24.

[6] *Analyst*, 34, 475.

Braun states that picramic acid is formed in these reactions. In the reduction of alkaline solutions of picric acid by creatinine, Chapman[2] holds that three stages of reduction are involved, *i. e.*, one, two, or three nitro groups are transformed to amino groups. We have observed that, whereas aldehydes, ketones, keto acids, creatinine, etc., give with alkaline solutions of picric acid a *red* color which usually is dissipated by an excess of the substance, the picrate product of reduction by sugars varies with increasing concentrations through yellow, red, brown to black, and is permanent, except toward light, in the presence of an excess of the substance oxidized.

Since the color[3] does not match closely with the colors of solutions of ferric acetate,[4] potassium bichromate, or *o*-nitrophenolate, we have adopted *the color of the sugar-picrate solution itself*, as the standard of color and thus, of course, obtain absolute identity of color.

Molecular equivalents of any available pure sugar, as sucrose, lactose, or glucose, may be used to make up the standard color solution. Since sucrose is anhydrous and can be obtained both cheaply and in the pure form, it is the best. However, since in the determination of the respective sugars, as for instance lactose and glucose, a reference to a particular sample of sugar may be desired, such sample may be made the standard with equal ease.

For convenience of calculation the solution used is best prepared so as to be read directly as *anhydrous monosaccharide*. Thus, for instance, to be equivalent to one gram of anhydrous glucose, the following quantities of other sugars[5] must be used:

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[1] *Chem. Zentr.*, **1847**, 623; *Lancet*, **25**, Sept., 1844; *Chem Ztg.*, **1901**, *Rep*, **209**; *Münch. med. Wochschr.*, **1906**, 1309.

[2] *Chem. News*, **100**, 175; *Brit. Med. J.*, Dec. 12, 1908.

[3] When an excess of glucose was heated with the picrate solution, afterwards cooled and then treated with dilute sulfuric acid, an amorphous precipitate was formed. It was filtered, washed with water, redissolved in alkali and reprecipitated by sulfuric acid. After washing first with water and then with alcohol, it was dried in a vacuum desiccator over sulfuric acid. Thus prepared, the substance was brown-black and did not melt at 270°. Since 4,6-dinitro-2-aminophenol melts at 169° and 2,6-dinitro-4-aminophenol melts at 170°, the substance cannot be either of these. Since the alkaline salt of triaminophenol gives, with ferric chloride, a violet color, while this substance does not, it cannot be the triamino compound With hot water the substance yields a difficultly soluble black residue and an easily soluble brown solute, hence it must be a mixture. Its composition will be investigated later.

[4] Johnson, *Pharm. J. and Trans.*, **54**, 24.

[5] For the preparation of pure sugars from commercial samples, see the following: *Sucrose*, THIS JOURNAL, **23**, 61; *U. S. Bur. Chem. Bull.*, **73**, 58; *Glucose*, Munson and

Sucrose	0.950
Glucose monohydrate	1.100
Lactose monohydrate	1.000
Lactose (anhydrous)	0.950
Lactose ($^1/_2$ mol H_2O)[1]	0.975

The picric acid solution is so prepared that it contains two grams of the acid and four grams of anhydrous sodium carbonate per liter; thus, in the color standard, twice as much picric acid as sugar is used. An excess of picric acid is necessary not only to insure complete oxidation of the sugar, but, as observed by Chapman, to prevent the formation of colorless reduction-products of the picric acid. On the other hand, too large an excess is to be avoided since it has an effect on the colorimetric reading.

Sodium carbonate, instead of sodium hydroxide,[2] is used because it avoids both the hydrolytic and the decomposing effect of the latter. In using the same concentration of different carbohydrates and treating under identical conditions, we have found that: (1) sodium carbonate solutions of picric acid at room temperatures give no increased color with carbohydrates, even after weeks' standing, except in the case of fructose, which slowly darkens; (2) *on boiling*, all sugars except sucrose and raffinose develop color immediately, with sodium carbonate solutions of picric acid; (3) sodium hydroxide solutions of picric acid, *at room temperature*, slowly develope color with all sugars and many other carbohydrates.

Preparation of Solutions.

(A) *The picrate solution* is prepared as described above.

(B) *The standard color solution* is prepared as follows: Dissolve 0.95 gram of pure cane sugar in about 100 cc. of water contained in a 500 cc. casserole and add 5 cc. of concentrated hydrochloric acid.[3] Heat on the water bath 15 minutes, dilute and cool, add an excess of sodium carbonate solution and 100 cc. of the picrate solution. Boil for 5 minutes after the color begins to develop and dilute to one liter. The color of this solution[4]

Walker, THIS JOURNAL, **28**, 667; *Lactose*, Lippman, *Die Chemie der Zuckerarten*, 3 Auflage, 1526; Walker, THIS JOURNAL, **29**, 541; *Maltose*, Walker, *Ibid.*, **29**, 542; also see *Ibid.*, **34**, 326.

[1] See THIS JOURNAL, **29**, 54.

[2] For the effect of alkalies on sugars, see especially: Benedict, *J biol Chem.*, **3**, 101; **5**, 485; Kendall, THIS JOURNAL, **34**, 317; McLean, *Biochem. J.*, **2**, 156; Jolle, *Z. Nahr. Genussm*, **20**, 631.

[3] For the hydrolysis of cane sugar, see Wiley's Agricultural Analysis, Vol. III, 105–107; Bornträger and Samelson, *Z. angew. Chem.*, **1892**, 334; **1893**, 690; **1894**, 267, 351; Munson and Walker, THIS JOURNAL, **28**, 667.

[4] This 0.1% solution of reduced picrate possesses nearly the same color and intensity of color as a 3% solution of potassium dichromate; it is nearly 30 times as intensely colored as the dichromate.

is equivalent to that produced by 1 gram (0.1%) of anhydrous monosaccharide per liter. This solution is too concentrated for use in the colorimeter; 100 cc. of it should be diluted to one liter (0.01%). For the "bottle standards" described below, however, it is the most convenient starting solution.

General Method of Manipulation.

Carefully weigh out approximately one gram of the carbohydrate or mixture of the same containing no interfering[1] substance. The monosaccharides, lactose and maltose react directly when heated with the picrate solution; hydrolyze sucrose and raffinose by adding 5 cc. of concentrated hydrochloric acid and heating for 15 minutes on the water bath. Neutralize with sodium carbonate solution and make up to one liter in a volumetric flask. Run exactly 10 cc. of this solution into a 100 cc. volumetric flask, add 10 cc. of the picrate solution and heat on the sand bath so that the solution boils for 5–10 minutes. Cool and add water to the 100 cc. mark. Place this solution in a standard colorimeter cylinder and adjust its depth to any depth of the standard color solution contained in the other colorimeter cylinder.

Calculation.—Divide the reading of depth of solution in the color-standard cylinder by the reading of depth of solution in the other cylinder and multiply by the weight of substance taken and the quotient[2] is *grams of anhydrous monosaccharide per liter.* The following table gives the factors necessary to convert to the other sugars or their hydrated forms:

Carbohydrate	Formula.	Mol. wt.	Factor.
Rhamnose........... ..	$C_6H_{12}O_5$	164.096	0.9111
Glucose...............	$C_6H_{12}O_6.H_2O$	198.112	1.1000
Glucose........	$C_6H_{12}O_6$	180.096	1.0000
Galactose.............	$C_6H_{12}O_6$	180.096	1.0000
Mannose............ .	$C_6H_{12}O_6$	180.096	1.0000
Fructose..............	$C_6H_{12}O_6$	180.096	1.0000
Maltose	$C_{12}H_{22}O_{11}.H_2O$	360.192	1.0000
Maltose...............	$C_{12}H_{22}O_{11}$	342.176	0.9500
Lactose............ .	$C_{12}H_{22}O_{11}.H_2O$	360.192	1.0000
Lactose...............	$C_{12}H_{22}O_{11}$	342.176	0.9500
Sucrose...............	$C_{12}H_{22}O_{11}$	342.176	0.9500
Raffinose	$C_{18}H_{32}O_{16}.5H_2O$	594.336	1.1000
Raffinose............ .	$C_{18}H_{32}O_{16}$	540.288	1.0000

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[1] The color of certain solutions, as of syrups, molasses, urine, etc., interfere; also polyphenols, aldehydes, ketones, purine bases, etc., will reduce the alkaline picrate solution. A systematic survey of compounds treated with alkaline picrate solution will be given later.

[2] It must be remembered that both the color standard and the unknown were first dissolved in one liter, then diluted to one-tenth concentration. If other dilutions of the color standard are used, the decimal point must, of course, be altered accordingly. In case of a low percentage of sugar in the unknown and when about 1 gram is used, it will be advantageous to dilute only to one liter.

Example.—When 1.0200 grams of a sample containing lactose and some indifferent substance was treated in the above-described manner, a reading of 25.5 mm. in the colorimeter cylinder was exactly matched by 20 mm. depth of the standard color solution contained in the other cylinder. That is 20/25.5 of 1.0200 is equal to 80% of anhydrous monosaccharide and this multiplied by 0.95 (see table) gives 76% of anhydrous lactose in the original sample.

Colorimeters and a Proposed Substitute.—Of course, any of the types of colorimeters may be used but Duboscq's is especially to be recommended. In the absence of a colorimeter, bottles of clear glass and of the same size and shape may be used. Square bottles of about 40 mm thickness and 60 cc. capacity are especially convenient, though nearly any uniformly shaped and sized bottle may be used.

From the standard color solution prepared as described above, solutions of the following percentage-concentrations are prepared.

0.1	0.09	0.08	0.07	0.06	0.05	0.04	0.03	0.02
0.01	0.009	0.008	0.007	0.006	0.005	0.004	0.003	0.002
0.001	0.0009	0.0008	0.0007	0.0006	0.0005	0.0004	0.0003	0.0002
0.0001	0.00009	0.00008	0.00007	0.00006	0.00005	0.00004	0.00003	0.00002

Since concentrations above 0.05% in the 40 mm. bottles are nearly opaque and below 0.0005% are nearly the same in color as the picrate solution, only "bottle standards" from 0.03% to 0.0005% need be prepared, that is, only seventeen in all, a task that need not consume more than two hours of time.

To use these "bottle standards," the carbohydrate of unknown concentration is treated as described above and its colored solution is placed in a bottle of the same size and shape as the color standard bottles, a little of the solution being first used to rinse out the bottle. A comparison is then made with the color standards. the bottles being placed on white paper and viewed from some distance. Viewing the bottles with nearly closed eyes and from distances of six or more feet is recommended, not only as involving no eye-strain but as enhancing the sensitiveness of reading. Attention is called to the fact that when the colors of the unknown and the standard appear identical if viewed transversely, a viewing of the same longitudinally will often show a difference. With a little practice the matching of the unknown with the standard may be made in a few moments.

Theoretically, in viewing two or three bottles *in tandem* and alongside of the bottle containing the unknown, any decimal of concentration from 0.05 down to 0.0005 may be read. In practice, to determine the concentration of the unknown, only one bottle standard or two *in tandem* are matched against the unknown. This results from the following conditions: (1) a finer reading is unnecessary for most analytical purposes; the digits indicating the concentrations give readings as parts per 10,000, 100,000 or 1,000,000; (2) in accordance with Weber's law of sensation, the eye is not sensitive[1] to all differences of concentration, especially in the upper part of a series.

Durability of the Color Standards.—Since the color standards are not strictly proof to sunlight they should be kept in the dark when not in use, However, the following data show that their rate of deterioration is slow. Series (A) was freshly prepared; series (B) was kept for twenty days in summer sunlight.

A.	B.	A.	B.	A.	B	A	B
0.070	0.080	0.020	0.033	0.008	0.013	0.0009	0.0015
0.060	0.070	0.018	0.030	0.007	0.012	0.0008	0.0012
0.050	0.060	0.016	0.025	0.006	0.010	0.0007	0.0009
0.045	0.060	0.015	0.023	0.005	0.008	0.0006	0.0008
0.040	0.055	0.014	0.020	0.004	0.006	0.0005	0.0006
0.035	0.050	0.012	0.018	0.003	0.0044	0.0004	0.0005
0.030	0.045	0.010	0.016	0.002	0.0030	0.0003	0.0004
0.025	0.035	0.009	0.015	0.001	0.0016	0.0002	0.0002

It will be observed that to match the respective concentrations of (A), invariably greater indicated concentrations of (B) were necessary, hence, with very old standards the analytical data will be too high. It is recommended that a stock solution of the color solution (0.1%) be prepared and preserved in the dark; from it new "bottle standards" may be prepared when necessary.

Colorimetric Readings by Artificial Light.—As is well known, the judging of shades of color by artificial light leads to error, especially in the case of yellows. Reds and browns are little liable to such error, hence the upper part of the color-standard series (the 0.05% to 0.0005% part recommended above) is adapted to use in artificial light. This is true for the reasons not only that the reds and browns are persistent but that the yellow of the excess of picrate solution, theoretically, at least, a disturbing influence, is reduced to *nil* in such light.

Accuracy of the Method.—Equal concentrations (0.1%) of the following carbohydrates were prepared and preserved with toluene: the polysaccharides were finely divided, suspended in water and shaken thoroughly before being measured out. Each was treated with the picrate solution in the manner described above and finally diluted to 0.01% concentration.

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[1] For discussion of variable sensitiveness in colorimetry see Horn and Blake, *Am. Chem. J.*, **35**, 253; **36**, 195, 516.

Carbohydrate.	Mols H_2O.	Standard.	Calc conc.	% error.
Glucose		0.01	0.01	.
Fructose		0.01	0.01	..
Galactose		0.01	0.01	.
Mannose		0.01	0.01	..
Rhamnose	1	0.01	0.0101	1.00
Maltose	1	0.0094	0.009895	1.05
Lactose	1	0.0095	0.01	
Sucrose		..	....	
Sucrose (hydrolyzed)	.	0.0105	0.009974	0.26
Raffinose	5	.	..	
Inulin		...	...	.
Dextrin		0.002	?	?

Lactose in Milk.—Measure out 10 cc. of milk and run it into a 250 cc. volumetric flask with 50 100 cc. of water and 1 cc. of 50% sulfuric acid. Heat on the sand bath until flocks of casein separate or until the mixture boils. Cool and add water to the 250 cc. mark. Pour upon a dry filter and, by means of a graduated pipet, take 6.25 cc. of the filtrate and run it into a 250 cc. volumetric flask. Add 2 3 volumes of water, an excess of sodium carbonate solution, and 10 cc. of the picrate solution. Heat on the sand bath five minutes after the color begins to develope. Cool and dilute to the 250 cc. mark. Estimate the color by the colorimeter or by means of the bottle standards. For the latter, rinse the bottle with some of the solution, then fill and compare with bottle standards. Multiply the percentage marked on the bottle standard by 1000 as the percentage of lactose in the milk.

Advantages of the Method.—A speedy and accurate *colorimetric* method for most carbohydrates is introduced.

Only one oxidizing solution, the picrate solution, is necessary and it is cheap, stable, easily prepared and need not be strictly quantitative.

The oxidizing solution is alkaline with sodium carbonate, avoiding secondary reactions on sugars produced by caustic alkali.

With the use of the bottle standards, the method is not only inexpensive but is easily within the reach of all working chemists.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERISTY OF WASHINGTON.]

A COMPARISON OF VARIOUS PRESERVATIVES OF URINE.

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In certain studies on normal urines, incurring the collection and keeping of hundreds of liters, the necessity of using a non-volatile preservative compelled us to test a number of reagents to determine their preservative power.

The ideal preservative for urine requires continuous conformity to the specifications (1) of being neutral or acidic and non-volatile, (2) of having efficient antiseptic power, (3) of being free from hydrolytic or other chemical effects on the organic components of urine and (4) of avoiding interference with reactions involved in the ordinary analysis of the urine.

Though no single preservative meets all of these requirements, a few approximate the same. However, it is scarcely to be expected that a solution so complex as urine, containing so many organic and inorganic compounds, held in acidic-basic, hydrolytic, precipitative, and oxidative equilibria, can be maintained indefinitely in its original composition. It is rather to be expected that one preservative will be effective with certain components of the mixture, while another preservative must be used for others. Hence a variety of preservatives must be studied and their modifying influences must be noted.

For our purpose sulfuric acid was finally adopted, but our studies led us so far afield that we determined to make a systematic survey of preservatives of urine, of which the following is of the nature of a preliminary report. This undertaking was further justified not only by the the fact that only a little work has been done, at least in a comparative manner, on preservatives of urine, but also for the reason that profound chemical changes resulted when urines were preserved with sulfuric acid and other reagents.

In the first set of experiments a quantity of urine, to which dextrose had been added, was hermetically sealed in flasks with the respective preservatives; the second set was put up in glass-stoppered bottles; all the samples were in 500 cc. volumes. After certain times the changes that resulted were observed (1) directly, (2) microscopically and (3) through chemical analysis.

Direct observation showed that all samples became cloudy or yielded precipitates on standing. Thymol remained clear the longest; the others gave cloudiness or precipitates immediately or after days, inversely in the order of formaldehyde, ether, toluene, hydrochloric acid, chloroform, etc. The following developed mold: hydrochloric acid, hydrogen peroxide, formaldehyde, boric acid and strychnine sulfate.

Microscopical examination showed that bacteria were present in all samples, and in large numbers, except in cases of hydrochloric acid and formaldehyde. Urate crystals were present in the sediments of all samples, but seemed to decrease in volume after many days in samples containing mold, especially in the case of hydrogen peroxide. All the urines, except those treated with strychnine sulfate, formaldehyde, toluene, thymol and sodium benzoate, being acidic in reaction, gave sediments containing calcium oxalate but no triple phosphate; the latter urines being alkaline gave both, except in the case of sodium benzoate which gave neither.

In the following tables are given the chemical data as percentages.

TABLE I.

No.	Preservative.	Grams per 500 cc.	Litmus[2]	Days[4]	Total phosphate.	Glucose.	Chlorine 174.[3]	Uric acid.	Ammonia.	Urea 176.[3]	Urea corr. 176[3].	Creatinine 173.[3]
..	None[1]...	..	A	..	0.1499	0 6896	..	0 0370	0.0136	..	...	..
..	None....	..	B	83	..	0.2439	0.7302		..	2.0890	..	0.1421
1	Salicylic acid.....	1	A	82	0.1350	0.6890	0 7372	..	0.0146	1 9631	0.938	0.8901
2	Chloroform........	3	A	18	0.1414	0.3827	0.8195*	0.0290	0 0158	1.0001	0.972	0.6231
3	Thymol........	1	B	53	0.1410	0.9524*	0.7411	..	0 0342	1.9621	0.902	0 9643*
4	Boric acid......	1	A	29	0 1370	0.5127	0.7681*	0.0350	0.0166	..	...	0.6750
5	Ether.....	1 6	A	52	0.1310	0 2777	0.7411	0 0150	0.0259	1.9361	0.891	0.9643*
6	Formaldehyde	2	B	51	0 1362	0 7093*	0 7380	0 0365	0.0300	1.8921	0.842	0.6639
7	H_2O_2 (3%)..	2	A	33	0.1458	0 4167	0 7018	0.0252	0.0311	1.9631	0.909	0.8901
8	HCl (conc.)........ ..	2 4	A	26	0 1385	0 2890	0 8585*	0.0310	0.0331	1.9441	0.886	0.9000
9	Toluene.	1 6	B	46	0.1350	0 9748*	0.7414	0 0370	0.0342	1.9481	0.888	0.8901
10	Sod. benzoate....	1	B	44	0 1375	0 3960	0.7459	0.0210	0.0411	1.0341	0.962	0.0040

[1] Analyzed on the day when the samples were put up.

[2] The letter A indicates acidic or neutral reaction; B indicates alkaline reaction.

[3] The numbers in the headings of these tables indicates days.

[4] The days of this column refer to the columns of phosphates, glucose, uric acid and ammonia. The days of preservation of others are given in the respective columns.

TABLE II.

No.	Preservative.	Grams per 500 cc.	Litmus.[2]	Glucose 20.[3]	Picrate 20[3]	Uric acid 163[3]	Ammonia 28.[3]	Urea 67.[3]	Urea corr. 67.[3]	Creatinine 29.[3]
.	None[1]	..	A	4 545	...	..	.	1.710	...	0.648
.	None	..	A	4 166	..	0 0080	0.0956	1.635	1.468	0.623
1	Salicylic acid	1	A	4 546	5 5	0 0134	0.0306	1 649	1 596	0.628
2	Chloroform	9	A	4.706*	6.0*	0 0246	0 0308	1 730	1.676	0.487
3	Thymol	1	A	4.420	5 5	0 0190	0 0242	1.700	1 658	0 575
4	Boric acid	1	A	4.255	5.7	0.0125	0 0325	1 643	1.586	0 506
5	Ether	16	A	4 469	5 1	0.0160	0.0319	1.744	1 688	0.566
11	Sod. arsenite	1	A	4 445	5 2	0 2200	0 0356	1 643	1.581	0 623
12	Sod. borate	1	A	4.211	5 4	0 0125	0 0343	1 610	1.530	0 416
13	Strychnine H_2SO_4	1	B	4.520	5 2	0.0040—	0 0220	1 627	1 589	0.529
14	Sulfuric acid	4	A	4 020	6 0*	0 0030—	0 0345	1.560	1 500	0 625*
14	Sulfuric acid	18	A	4.082	5 8	0 0020—	0 0241	1 287	1 245	0 000*
15	Phenol	1	A	4.494	7 0*	0 0130	0 0355	1 600	1.538	0.675*
16	Gallic acid	1	A	4 706*	6.2*	0 0620	0 0310	1 632	1.578	..
17	Sandalwood oil	1	A	4.566	5 5	..	0.0225	. .	...	0 506

[1] Analyzed on the day when the samples were put up.

[2] The letter A indicates acidic or neutral reaction; B indicates alkaline reaction.

[3] The numbers in the headings of these tables indicate days.

The total phosphate was determined by the uranium acetate method; the glucose by Purdy's method; the ammonia and creatinine, by Folin's methods; the uric acid, by Ruhemann's method;[1] the urea and chlorine, by Dehn's methods;[2] and the total reduction of alkaline picrate by boiling and estimating colorimetrically.[3]

These analytical methods, except for phosphates and for chlorine, are subject to criticisms. The determination by Purdy's solution includes other oxidation-reactions besides glucose; the aeration of alkaline urines yields other volatile bases besides ammonia; the development of color in cold as well as hot alkaline solutions of picric results from other substances besides creatinine; and with hypobromite, nitrogen is evolved from ammonia as well as from urea. We have corrected for ammonia in the urea reading by multiplying the percentages of the former by 1.75 and subtracting this from the percentages of the latter.

Though some of these methods are known to be somewhat inaccurate, for our purposes, being rapid and applied under the same conditions, they give valuable and comparable data.

Observations drawn from the above tables of data are made upon (1) abnormal indications, (2) effects upon the respective components of urine and (3) estimates of the respective preservatives.

Abnormal Indications.—The most important abnormal indications are such as are produced on the analytical data by the preservatives themselves. These are marked in the tables with the asterisk, at least those that are very apparent and whose causes are evident are so marked. However, it must be remembered that an apparent increase of concentration, owing to quantitative disturbances by the preservative, may be compensated by the loss of material, owing to fermentation and other causes. Therefore, when both factors are operative, the apparent reading of concentration may be above, equal to, or below the original concentration, but is invariably above the true concentration.

Since chloroform yields formic and hydrochloric acids by hydrolysis after standing, its presence vitiates chlorine and glucose determinations. Other preservatives that destroy the accuracy of glucose are gallic acid, phenol, salicylic acid, formaldehyde,[4] hydrogen peroxide, and thymol.[5]

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[1] *Berl. klin. Wochsch.*, **1903**, Nos 2 and 3; *Deut. med. Z*, **1903**, No. 8; *Med Woch.*, **1904**, No. 3.

[2] *Z. anal. Chem.*, **44**, 604; *Z. physiol. Chem.*, **44**, 11.

[3] We have found that hot alkaline solutions of picric acid develops color not only with creatinine but also with glucose, uric acid, other purine bases, acetone and acetoacetic ester. We are investigating the possibility of application of this reaction to the analysis of urine. See preceding article.

[4] For the effect of formaldehyde on Fehling's solution see Rudd and Bolenbaugh, Proc. Virginia Chemists' Club, 220.

[5] For the effect of thymol on acetone see Welker. *J. Biol. Chem.*, **3**, 27; *N. Y. Med. J.*, **86**, 552.

Since thymol also absorbs iodine and reduces alkaline picrate solutions, its presence will effect not only the glucose, but also the uric acid and creatinine determinations. Owing to hydrolysis, sulfuric acid, in dilute concentrations, converts creatine into creatinine; in greater concentrations sulfuric acid precipitates the creatinine. For these reasons sulfuric acid gives the abnormal results indicated above. All concentrations of sulfuric acid not only effect the creatinine but precipitate the uric acid and most of the coloring matter of urine.

Adequate explanations of the other high results in the tables are impossible at present.

Changes in Urine.—The changes possible in urine through aging and standing with preservatives are almost as numerous as the components of the mixture. Only certain inorganic salts, as for instance sodium chloride, seem proof to chemical decomposition. The easiest observed changes result from mere cooling, when urates and other substances are precipitated. A change in reactivity, as when normally acidic urine become alkaline, is accompanied by numerous chemical transformations, particularly of the urate, the phosphate, and the creatine-creatinine equilibria. For this reason it is evident that an acid preservative most often will be the more desirable.

Important transformations in urine are produced bacterially on glucose, urea and other fermentable substances. The enzymes developed are chemically hydrolytic, dissociative and oxidative, as evidenced by the formation of alcohol, carbon dioxide, ammonia, nitrite and nitrate. Though each of the preservatives in the above studied concentrations, undoubtedly has inhibitory influence, none has perfect bactericidal power, hence none is a perfect preservative.

Reference to the above data shows very little change in the phosphates, except when the reaction of the solution becomes neutral or alkaline; a notable exception is the ether sample. The chlorine analyses are uniformly constant, except when interfered with by such preservatives as hydrochloric acid, hydrogen peroxide, and chloroform; why the boric acid sample is high is not evident. With glucose the compensating influence of the preservatives and loss by fermentation are evident in cases of chloroform, thymol and gallic acid; probably with phenol, sodium arsenite and ether also. Salicylic acid, sandalwood oil and boric acid seem best for the preservation of dextrose. With uric acid, the changes are apparently great with ether, hydrogen peroxide and sodium benzoate; however, it must be remembered that these preservatives, and also thymol, interfere with the analysis of uric acid by the uricometer method, thus giving rise to the discordant data.

The ammonia data, as direct estimates of the hydrolysis of urea, are probably the best indications of the comparative antiseptic value of the different preservatives, not only on account of the refinement of analysis of ammonia but also on account of the non-interference of preservatives with its determination. However, it must be remarked, that, although sulfuric acid yields but little ammonia, it transforms, possibly by oxidation, exceptional quantities of urea.

Considerable uniformity is met with in the analysis of urea, sulfuric acid alone seeming to have large destructive effect and formaldehyde being next with low results on account of precipitation.[1]

With creatinine there may be either an increase or a decrease of concentration. The increase resulting in acidic solutions involves the hydrolysis of creatine to creatinine. Since the colorimetric method of analysis of creatinine was employed, preservatives like thymol, phenol, ether, etc., gave too large readings of concentration. The decrease, resulting usually from the alkalinity of the solution, involves a transformation of creatinine to creatine; a decrease may also result, through precipitation, as in the treatment with sulfuric acid,[2]

The Respective Preservatives.—(1) Salicylic acid is the best preservative of those studied. This excellence of salicylic acid for urine was described by Jordan.[3] It is of further interest to observe that, finding alkaline salicylate to have no reducing or solvent effect on copper, Kendall[4] uses it instead of alkaline tartrate as the medium for oxidation of sugars. Its use, therefore, as a preservative will not interfere with the estimation of dextrose in urine by copper solutions.

(2) Though chloroform preserves urea, and therefore ammonia, it is ineffective with glucose and creatinine.[5]

(3) Thymol, though used frequently as a preservative for urine, does not seem to merit the value placed upon it; for, although little sediment is formed when it is used, and even if it had considerable bactericidal power, which is doubtful, its presence interferes with too many reactions involved in urine analysis. Gill and Grindley[6] made extensive studies on the preservation of urine by thymol and refrigeration and obtained good results for periods up to thirty-two days. However, it is very prob-

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[1] Vide infra.

[2] Edlefsen, *Münch. med. Wochsch*, **55**, 1615, 2524.

[3] *Biochem. J*, **5**, 274; *Proc Roy Soc. Med. Pharm. Sec.*, **5**, 26 See also Luchrig and Sartori, *Pharm. Centrh*, **49**, 934; Dafert and Haas, *Arch Chem Mikros*, **1908**, 1; E. von Meyer and H. Kolbe *J. prakt Chem*, **12**, 178

[4] THIS JOURNAL, **34**, 320.

[5] The loss of creatinine when chloroform was used as a preservative was observed by Benedict and Myers, *Am. J. Physiol.*, **18**, 380. See also Gill and Grindley, THIS JOURNAL, **31**, 707. The unsatisfactory preservative power of chloroform for sewage was remarked by Lederet and Hommon, *Eng. Record*, **62**, 319; *J. Am. Pub Health Assoc.*, **1**, 267.

[6] THIS JOURNAL, **31**, 695; Hawk and Grindley, *Proc. Am. Soc. Biol. Chem.*, **9**, 10 (1907–8).

able that the *cold* and not the thymol was more important in the preservation of the urines studied.

(4) Boric acid has little merit[1] as a preservative of urine, at least in 0.2% concentration.

(5) Ether in large quantities preserves well, but volumetric relations are thereby disturbed.

(6) Formaldehyde cannot be considered a good preservative, because it precipitates urea[2] and is a reducing substance.

(7) Hydrogen peroxide (and its stabilizer) interferes with many reactions in urine analysis and has feeble bactericidal power.[3]

(8) Hydrochloric acid has nothing to recommend it as a urinary preservative.

(9) Toluene preserves uric acid and creatinine well.

(10) Sodium benzoate is a very poor[4] preservative of urine.

(11) Sodium arsenite is a fair preservative of urine.

(12) Sodium borate is a poor preservative of urine.

(13) Strychnine sulfate[5] is a good urinary preservative.

(14) Sulfuric acid has no value as a general preservative of urine; it causes too many reactions of hydrolysis and oxidation and does not prevent bacterial change.

(15) Since many bacteria are phenol-forming,[6] phenol cannot be expected to have much preservative power; moreover, it interferes with the analysis of many components of urine.

(16) Gallic acid has no value as a preservative of urine.

(17) Sandalwood oil, from the limited data given, indicates value as a preservative.

Summary.

(1) The ideal preservative must be soluble, non-volatile, and neutral or slightly acidic.

(2) Different preservatives must be employed for different purposes; no one preservative can prevent the change of all the components.

(3) The following may be considered poor preservatives of urine: for-

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[1] For the feeble inhibitory action of boric acid on diastatic ferments see Agullion, *Compt. rend.*, **148**, 1340; *Ann. inst. Pasteur*, **24**, 495. For other feeble preservative powers see Kuehle, *Pharm. Centr.*, **50**, 559; Luchrig and Sartori, *Ibid.*, **49**, 934.

[2] Goldschmidt, *Ber.*, **29**, 1896; May, *Deut. Arch. klin. Med.*, **1900**; de Jager, *Z. physiol. Chem.*, **64**, 110. For bacterial resistance to formaldehyde, Tiraboschi, *Il policlin.*, **15**, 39, 40.

[3] Croner, *Z. Hyg.*, **63**, 319.

[4] For the action of sodium benzoate on bacteria, Herter, *J. biol. Chem.*, **7**, 59; see also, Lucas, *Proc. Soc. Exp. Biol. Med.*, **6**, 122.

[5] For the effective influence of strychnine on bacteria see Scadikow, *Centr. Bakt. Parasitenk. I Abt.*, **60**, 417.

[6] Dobravotski, *Ann. Inst. Pasteur*, **24**, 595.

maldehyde, hydrogen peroxide, phenol, boric, gallic, hydrochloric and sulfuric acids, sodium borate and sodium benzoate.

(4) The following are better preservatives: chloroform, toluene, ether and thymol.

(5) The best preservatives are salicylic acid, strychnine sulfate, sodium arsenite and probably sandalwood oil.

SEATTLE, WASH.

[FROM THE CHEMICAL SECTION OF THE IOWA AGRICULTURAL EXPERIMENT STATION.]

THE EFFECT OF ACIDS AND ALKALIES UPON THE CATALASE OF TAKA-DIASTASE.

BY RAY E. NEIDIG

Received December 22, 1913.

It is well known that extracts from plant and animal tissues contain catalase, an enzyme capable of decomposing hydrogen peroxide. The effect of acids and bases toward this enzyme has been the subject of numerous investigations. In this field, Jacobson[1] was the first to note that acid caused a retarding effect upon solutions of catalase obtained from blood. Later, Senter[2] made a more exhaustive study of blood catalase, in which he determined the effect of three acids, namely, hydrochloric, nitric and acetic, and also of sodium hydroxide upon this enzyme. From this investigation he concluded that the time of contact of the acid with the catalase solution had very little influence upon the reaction, that there was no decomposition of the enzyme during its contact with acid, and, lastly, that neutralization of the acid restored the original activity of the catalase. Sodium hydroxide, he found, exercised an inhibiting effect similar to that of acids.

As these first two investigators dealt wholly with catalase from blood, Euler[3] undertook an investigation to determine whether or not catalase from different sources was identical. His work included catalase from one of the higher fungi, *viz.*, *Boletus scaber*. He found an important difference between the action of acids on the inhibition of the catalase obtained from *Boletus scaber* and that obtained from blood (Senter),[4] tobacco extract (Loew),[5] and yeast (Issaew).[6] He also observed that freshly precipitated magnesium hydroxide greatly increased the catalytic power of the enzyme. In this observation he corroborated the work of Loew,[4] who noted the same increase in enzymic activity when magnesium hydroxide was added to extracts of tobacco.

[1] *Z. physiol. Chem.*, **16**, 340.

[2] *Ibid.*, **44**, 257 (1903).

[3] *Hofm. Beitr.*, **7**, 1 (1905).

[4] *Loc. cit.*

[5] U. S. Dept. of Agr., *Report No.* 68.

[6] *Z. physiol. Chem.*, **42**, 102 (1904).

In view of the results obtained by Euler, the writer thought it of interest to study the effect of a number of the more important acids and alkalies upon catalase obtained from lower fungi. It has been shown by Bach and Chodat[1] that cultures of *Sterigmatocystis nigra* contain catalase. Pringsheim[2] demonstrated catalase in the pressed juice of fifteen out of seventeen molds studied by him. Dox[3] has shown that catalase was present in the filtrate of thirty-four out of thirty-five molds which he examined, and Loew[4] observed that the filtrate from *Pencillium glaucum* showed the power of decomposing hydrogen peroxide, and also that the commercial taka-diastase, an enzyme preparation of high purity made from the fungus *Aspergillus oryzae*, is also rich in catalase. It occurred to the writer that, owing to the high degree of purity of the commercial taka-diastase, this enzyme preparation would be an excellent source of material to use in a study on the catalase of lower fungi.

Experimental.

The methods and apparatus used in determining the strength of catalase are numerous and will not be reviewed in detail here. The principle on which the methods are based is the determination of the amount of free oxygen liberated when a solution containing catalase is brought in contact with hydrogen peroxide. This is commonly performed by collecting over water the oxygen given off and reducing the results to 0° and 760 mm. pressure, or by measuring the amount of pressure developed by means of a manometer, and lastly, by titrating the undecomposed hydrogen peroxide with a standard solution of potassium permanganate.

Van Slyke's amino nitrogen apparatus was used in the determinations, and found to be very satisfactory where the enzyme solution is comparatively pure. The advantages of this apparatus over many others are: (1) its ease of manipulation, and (2) the uniformity of results obtained by maintaining a constant rate of agitation during the reaction between enzyme and peroxide. That the speed of shaking has a direct influence upon the amount of oxygen liberated during a given time was previously shown by Loew and confirmed by the writer in the following experiment:

To each of two equal portions of enzyme solution in the apparatus were added three cubic centimeters of hydrogen peroxide. The total oxygen given off was noted at the end of ten minutes:

(1) with shaking...	33.6 cc. oxygen
(2) without shaking......................	23.5 cc. oxygen

While shaking the enzyme solution the apparatus averaged 140 oscillations per minute. The same speed was maintained as nearly as possible throughout the following determinations:

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[1] *Ber.*, 36, 1756 (1893).

[2] *Z. physiol. Chem.*, 62, 386 (1909).

[3] THIS JOURNAL, 32 (Oct., 1910).

[4] *Loc. cit.*

The enzyme solution used in this work was prepared by dissolving 0.625 gram of the commercial taka-diastase in 100 cc. of water. After filtering, ten cc. of this solution were diluted so that, when the required amount of acid was added, the total volume of the solution was 15 cc. Throughout the work, unless otherwise stated, the time of contact of an acid with the enzyme solution was fifteen minutes and at the end of that time the solution was diluted with distilled water to 22 cc. and then brought in contact with 3 cc. of hydrogen peroxide. The volume of oxygen developed was read at the end of each minute for a period of ten minutes. As a control experiment the same procedure was followed except that the acid was omitted. A similar experiment was made to ascertain the effect of neutralization of the acid on the enzyme activity after fifteen minutes' contact with the enzyme solution. This was accomplished by adding to the acid solution the exact required amount of standard sodium hydroxide, then making the volume up to 22 cc. and mixing the solution with 3 cc. hydrogen peroxide, noting the volume of oxygen developed each minute for a period of ten minutes. The tables follow:

TABLE I.[1]

Effect of 15-Minute Contact with 0.1*N* H_2SO_4.

Time after adding H_2O_2 [2] (Minutes.)	0.1 *N* H_2SO_4 added.						
	0 cc.	0.2 cc	0.4 cc.	0.8 cc.	1.2 cc.	1.4 cc	1.6 cc.
	Oxygen developed						
1	9.2	8.6	8.0	4.6	1.3	trace	0.0
2	15.9	15.4	14.0	9.7	3.2	0.3	0.0
3	20.7	19.6	18.3	13.8	4.4	0.4	0.0
4	24.5	22.9	21.3	16.6	5.1	0.5	0.0
5	26.6	25.0	23.4	18.6	5.6	0.6	0.0
6	28.1	26.9	25.0	19.9	5.9	0.7	0.0
7	29.4	28.4	26.4	20.8	6.3	0.8	0.0
8	30.3	29.5	27.4	21.5	6.6	0.8	0.0
9	31.1	30.5	28.3	22.0	6.6	0.8	0.0
10	31.8	31.2	28.9	22.4	6.7	0.8	0.0

Effect of Neutralization of H_2SO_4 after 15-Minute Contact.

1	9.2	9.2	7.9	5.3	1.4	trace	0.0
2	15.9	15.9	14.6	11.2	3.8	0.5	0.0
3	20.7	20.9	19.2	15.0	5.5	1.0	0.0
4	24.5	23.7	22.4	17.4	6.5	1.2	0.0
5	26.6	25.7	24.6	18.8	7.8	1.5	0.0
6	28.1	27.7	26.4	20.1	8.3	1.8	0.0
7	29.4	28.9	27.7	21.1	8.8	2.0	0.0
8	30.3	30.0	28.7	22.0	9.1	2.2	0.0
9	31.1	30.8	29.7	22.6	9.3	2.4	0.0
10	31.8	31.5	30.5	23.2	9.5	2.5	0.0

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[1] All the volumes given in this paper are reduced to 0° and 760 mm. pressure.

[2] The hydrogen peroxide used contained 3.81% oxygen by weight or 12.54% by volume.

The results are illustrated graphically by the following curves: Fig. 1 illustrates the rate of liberation of oxygen during the first ten minutes, after 15-minutes contact with hydrogen peroxide and for the various de-

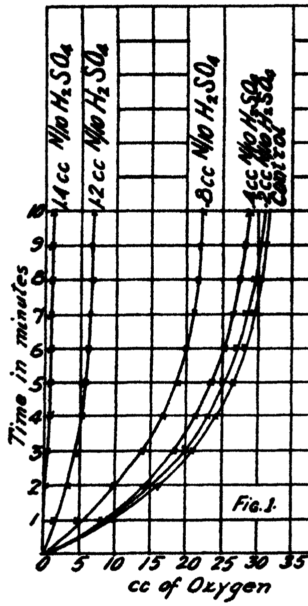

Fig. 1.

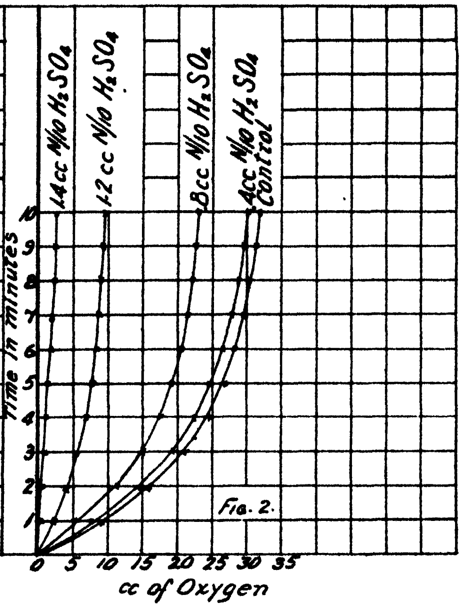

Fig. 2.

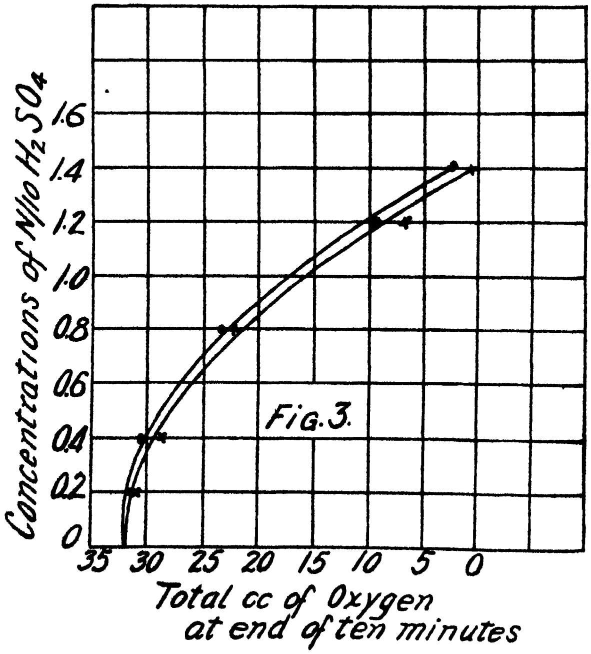

Fig. 3.

TABLE II.

Effect of 15-Minute Contact with 0.1 *N* HCl.

Time after adding H_2O_2. (Minutes)	0.1 *N* HCl added						
	0 cc.	0.2 cc	0.4 cc	0.8 cc.	1.2 cc	1.4 cc	1.6 cc.
	Oxygen developed						
1	8.8	7.8	7.6	2.5	0.9	trace	0.0
2	15.9	14.9	15.8	7.2	2.5	trace	0.0
3	21.0	20.0	20.7	10.8	3.6	trace	0.0
4	25.0	23.6	24.1	13.9	4.7	0.3	0.0
5	27.4	26.1	26.3	16.1	5.5	0.4	0.0
6	29.3	28.0	28.1	17.7	6.3	0.4	0.0
7	30.8	29.3	29.4	19.1	6.9	0.5	0.0
8	31.8	30.3	30.6	20.2	7.4	0.6	0.0
9	32.6	31.2	31.5	21.1	7.9	0.7	0.0
10	33.2	31.8	32.0	21.8	8.3	0.8	0.0

Effect of Neutralization of HCl after 15-Minute Contact.

1	8.8	8.0	7.6	3.6	2.1	0.0	0.0
2	15.9	15.2	14.9	9.1	4.8	trace	0.0
3	21.0	20.3	20.3	13.7	7.3	trace	0.0
4	25.0	23.6	23.9	17.2	9.5	0.4	0.0
5	27.4	26.1	26.5	20.0	11.6	0.5	0.0
6	29.3	28.0	28.1	21.8	13.2	0.7	0.0
7	30.8	29.3	29.5	23.6	14.4	0.9	0.0
8	31.8	30.3	30.6	24.9	15.5	1.0	0.0
9	32.6	31.1	31.5	25.9	16.4	1.0	0.0
10	33.2	31.8	32.2	26.8	17.0	1.1	0.0

TABLE III.

Effect of 15-Minute Contact with 0.1 *N* Oxalic Acid.

Time after adding H_2O_2. (Minutes.)	0.1 *N* oxalic acid added						
	0 cc	0.4 cc	0.8 cc	1.6 cc.	2 cc.	2.4 cc.	2.6 cc.
	Oxygen developed						
1	8.9	8.2	6.5	3.4	0.7	trace	0.0
2	15.9	15.8	12.6	7.0	1.8	0.2	0.0
3	20.8	21.3	17.0	9.6	2.8	0.4	0.0
4	24.1	24.1	19.7	11.5	3.8	0.5	trace
5	26.0	26.0	21.5	12.9	4.7	0.7	trace
6	27.3	27.7	22.8	14.0	5.5	0.9	trace
7	28.5	29.0	23.8	14.9	6.2	1.0	trace
8	29.5	30.0	24.6	15.5	6.7	1.1	trace
9	30.4	31.0	25.3	16.0	7.3	1.2	0.4
10	31.1	31.7	25.8	16.4	7.6	1.3	0.4

Effect of Neutralization of Oxalic Acid after 15-Minute Contact

1	8.9	8.4	7.3	5.3	2.1	0.7	0.0
2	15.9	15.8	14.1	10.3	3.9	1.7	0.0
3	20.8	20.1	18.5	13.9	5.7	2.6	0.0
4	24.1	23.1	21.4	16.1	7.2	3.4	trace
5	26.0	25.0	23.4	17.5	8.7	4.2	trace
6	27.3	26.4	24.8	18.5	9.9	4.8	trace
7	28.5	27.4	25.9	19.4	10.9	5.3	trace
8	29.5	28.3	26.9	20.1	11.7	5.7	trace
9	30.4	29.0	27.4	20.6	12.4	6.0	trace
10	31.1	29.5	28.0	21.1	13.0	6.3	trace

TABLE IV.

Effect of 15-Minute Contact with Normal Tartaric Acid.

Time after adding H_2O_2. (Minutes.)	Normal tartaric acid added.					
	0 cc.	0.1 cc.	0.2 cc.	0.4 cc.	0.6 cc.	0.8 cc.
			Oxygen developed.			
1	9.1	7.8	4.4	2.7	0.8	trace
2	15.7	14.7	9.3	6.1	1.7	0.2
3	20.2	18.7	13.0	8.4	2.8	0.5
4	23.4	21.0	15.5	9.8	3.6	0.7
5	25.6	22.8	16.9	10.8	4.3	0.8
6	27.2	24.0	18.0	11.4	4.8	0.8
7	28.5	24.8	18.8	11.9	5.2	0.9
8	29.5	25.7	19.6	12.2	5.6	0.9
9	30.2	26.5	19.9	12.5	5.8	0.9
10	31.0	26.8	20.3	12.7	6.1	0.9

Effect of Neutralization of Tartaric Acid after 15-Minute Contact.

Time after adding H_2O_2. (Minutes.)	0 cc.	0.1 cc.	0.2 cc.	0.4 cc.	0.6 cc.	0.8 cc.
1	9.1	7.8	5.3	5.4	1.3	0.8
2	15.7	15.2	10.6	8.8	2.7	1.0
3	20.2	20.2	14.4	11.1	3.9	1.3
4	23.4	21.7	17.2	12.8	4.9	1.7
5	25.6	23.3	19.1	14.0	5.7	1.9
6	27.2	24.6	20.6	14.8	6.4	1.9
7	28.5	25.4	21.8	15.5	7.1	2.1
8	29.5	26.2	22.7	16.1	7.6	2.2
9	30.2	26.9	23.5	16.5	8.1	2.3
10	31.0	27.4	24.1	16.9	8.6	2.3

TABLE V.

Effect of 15-Minute Contact with Normal Citric Acid.

Time after adding H_2O_2. (Minutes.)	Normal citric acid added.						
	0 cc.	0.2 cc.	0.4 cc.	0.8 cc.	1.2 cc	1.6 cc.	1.8 cc
			Oxygen developed.				
1	10.3	6.6	5.0	2.9	1.0	trace	0.0
2	16.6	13.2	9.9	6.0	2.0	0.3	0.0
3	20.7	17.7	13.5	7.4	3.1	0.5	0.0
4	23.8	20.1	15.7	8.3	4.1	0.8	0.0
5	25.7	21.8	17.2	8.9	4.9	0.9	0.0
6	27.3	23.0	18.3	9.3	5.5	1.0	0.0
7	28.4	23.9	19.0	9.6	6.1	1.0	trace
8	29.2	24.7	19.6	9.8	6.7	1.1	trace
9	30.0	25.2	20.1	9.9	7.0	1.2	trace
10	30.7	25.7	20.4	10.1	7.3	1.3	trace

Effect of Neutralization of Citric Acid after 15-Minute Contact.

Time after adding H_2O_2. (Minutes.)	0 cc.	0.2 cc.	0.4 cc.	0.8 cc.	1.2 cc	1.6 cc.	1.8 cc
1	10.3	8.4	6.5	4.2	1.1	trace	trace
2	16.6	14.6	11.8	7.9	2.7	0.3	trace
3	20.7	18.5	15.1	10.2	3.8	0.5	0.2
4	23.8	20.9	17.4	11.7	4.8	0.6	0.3
5	25.7	22.4	18.9	12.7	5.8	0.8	0.3
6	27.3	23.0	20.0	13.4	6.7	1.0	0.4
7	28.4	24.6	20.8	13.9	7.3	1.0	0.4
8	29.2	25.2	21.4	14.3	7.8	1.1	0.5
9	30.0	25.8	21.9	14.6	8.1	1.2	0.5
10	30.7	26.4	22.3	15.0	8.4	1.3	0.6

Table VI.

Effect of 15-Minute Contact with Normal Acetic Acid.

Time after adding H_2O_2. (Minutes.)	Normal acetic acid added.						
	0 cc.	0.5 cc.	1.5 cc.	4.5 cc.	6 cc.	8 cc	10 cc.
	Oxygen developed.						
1	9.0	4.2	2.4	0.6	0.3	trace	0.0
2	16.2	9.6	6.4	2.2	1.0	0.3	0.0
3	21.7	14.0	9.3	3.6	1.2	0.4	0 0
4	25.1	17.3	12.1	4.7	1.5	0.7	trace
5	27.8	20.0	13.8	4.5	1.8	0.9	trace
6	29.7	22.0	15.9	6.3	2.2	1.0	0.2
7	31.1	23.4	17.2	7.0	2.5	1.1	0.3
8	32.1	24.6	18.4	7.7	2.9	1.2	0.4
9	32.9	25.6	19.4	8.4	3.1	1.3	0.4
10	33.5	26.4	20 3	8.9	3.4	1.4	0.4

Effect of Neutralization of Acetic Acid after 15-Minute Contact.

1	9.0	6.9	6.9	4.9	2.0	1.4	1.2
2	16.2	13.3	12.4	8.4	5.1	3.2	2 3
3	21.7	19.8	16.7	11.7	7.6	4.7	3.3
4	25.1	23.3	20.0	13.8	9.3	5.8	4.0
5	27.8	25.5	21.9	15.5	10.5	6.6	4.7
6	29.7	26.9	23.1	16.6	11.5	7.2	5.2
7	31.1	27.5	24.2	17 3	12.2	7 7	5 7
8	32.1	29.0	25.1	18.0	12.7	8.0	6 1
9	32.9	29.9	25.9	18.5	13.1	8.3	6.3
10	33.5	30.9	26.5	19.0	13.5	8.4	6.4

grees of acid concentrations. The curves shown in Fig. 2 are analogous to those in Fig. 1 except that the determination was made after exactly neutralizing with sodium hydroxide.

Curve *a*, Fig. 3 shows the total volume of oxygen developed during the first ten minutes after 15-minute contact with different acid concentrations. Curve *b* in the same figure represents similar determinations after neutralizing the acid with sodium hydroxide. A comparison of these two curves shows that the effect of neutralization is very slight. The curves for the remaining acids show the same general characteristics and will not be included here.

The foregoing experiments show the relative inhibiting effect of acids toward catalase, when in contact with the enzyme solution for fifteen minutes. In order to ascertain the inhibiting effect of acids, when brought in contact with the enzyme solution for different periods of time, the following experiments were performed:

Different strengths of two of the inorganic acids were allowed to remain in contact with the taka-diastase solution for 0, 15, 30, and 60 minutes. The acids used were decinormal sulfuric (0.8 cc.) and hydrochloric (0.4 cc.), respectively. The activities of the catalase solutions were then determined in the usual manner.

TABLE VII.

Effect of 0.4 cc. 0.1 *N* HCl for Different Periods of Contact.

Time after adding H_2O_2. Minutes.)	Control.	0.4 cc. 0.1 *N* HCl added. Time of contact in minutes.			
		0.	15.	30.	60.
		Oxygen developed.			
1	7.9	5.1	5.2	4.9	5.1
2	14.2	10.9	11.0	10.8	10.3
3	18.5	15.2	15.6	15.5	15.1
4	21.8	18.6	19.2	18.7	18.7
5	24.5	21.8	21.8	22.1	21.2
6	26.7	24.1	24.0	23.9	23.6
7	29.3	25.6	25.7	25.6	25.6
8	29.8	26.8	27.0	26.7	26.9
9	30.9	27.9	28.2	28.1	28.0
10	31.8	28.9	29.0	29.0	28.7

TABLE VIII.

Effect of 0.8 cc. 0.1 *N* H_2SO_4 for Different Periods of Contact.

Time after adding H_2O_2. (Minutes.)	Control.	0.8 cc. 0.1 *N* H_2SO_4 added. Time of contact in minutes.			
		0.	15.	30.	60.
		Oxygen developed.			
1	7.4	2.8	2.1	2.1	2.0
2	13.7	6.9	5.5	5.7	4.8
3	18.3	10.6	8.8	8.8	7.5
4	22.1	13.1	11.4	11.5	10.1
5	25.5	15.4	14.3	14.7	11.8
6	27.8	16.9	15.0	15.6	14.0
7	29.6	18.4	16.5	16.9	14.5
8	30.9	19.3	17.4	18.1	15.8
9	31.9	20.1	18.3	19.2	16.5
10	32.7	20.8	19.0	19.9	17.2

The effect of acids toward the catalase of taka-diastase as shown by the preceding tables is very marked. In the series of acids studied none were found which did not show some inhibiting action. The inhibition, however, was not constant, equinormal solutions of different acids showing different power of inhibition toward the enzyme solution. The acids, arranged in order of the magnitude of their inhibiting effect, are hydrochloric, sulfuric, oxalic, tartaric, citric and acetic. It will be noted that this order corresponds to the order of their ionization constants.

Neutralization of the acid restored the enzyme activity only to a slight extent. In this respect catalase from taka-diastase differes from blood catalase. According to Senter, neutralization of the acid restores the original activity of the latter enzyme.

It has been shown above that the time, in which sulfuric and hydrochloric acids are in contact with the enzyme solution, has little or no effect upon the activity of catalase. The time of contact for the remaining

TABLE IX.

Effect of 15-Minute Contact with Normal KOH

Time after adding H_2O_2. (Minutes)	Normal KOH added.					
	0 cc	0 1 cc.	0 2 cc	0 4 cc	0 6 cc	0 8 cc.
	Oxygen developed					
1	8.2	6.4	4.1	1.3	0.3	0.0
2	14.4	11.9	8.6	2.8	0.4	0.0
3	18.9	16.3	12.5	4.2	0.7	trace
4	22.3	19.4	15.4	5.5	1.1	trace
5	24.9	22.0	17.7	6.6	1.4	0.2
6	27.1	23.8	19.3	7.4	1.6	0.3
7	28.8	25.6	20.6	8.1	1.7	0.3
8	30.3	26.5	21.7	8.7	1.7	0.4
9	31.3	27.5	22.5	9.1	1.8	0.4
10	32.1	29.0	23.3	9.5	1.9	0.4

Effect of Neutralization of Normal KOH after 15-Minute Contact.

Time after adding H_2O_2. (Minutes)	0 cc	0 1 cc.	0 2 cc	0 4 cc	0 6 cc	0 8 cc.
1	8.2	6.0	3.9	0.9	trace	0.0
2	14.4	11.3	7.9	2.5	0.2	0.0
3	18.9	14.6	10.9	3.5	0.4	trace
4	22.3	16.8	13.0	4.3	0.5	trace
5	24.9	18.8	14.4	4.9	0.6	trace
6	27.1	20.6	15.5	5.3	0.7	trace
7	28.8	22.0	16.4	5.7	0.8	trace
8	30.3	23.2	17.1	6.0	0.9	trace
9	31.3	24.1	17.9	6.2	0.9	trace
10	32.1	24.9	18.5	6.4	0.9	trace

TABLE X.

Effect of 15-Minute Contact with Normal NaOH.

Time after adding H_2O_2. (Minutes.)	Normal NaOH added.					
	0 cc.	0.1 cc.	0.2 cc.	0 4 cc.	0 6 cc.	0 8 cc.
	Oxygen developed.					
1	9.4	6.4	6.1	1.7	0.0	0.0
2	15.8	12.2	10.5	2.6	trace	0.0
3	20.2	16.3	14.1	3.8	0.4	0.0
4	23.5	19.5	16.8	4.4	0.7	0.0
5	25.7	21.8	18.8	4.9	0.9	0.0
6	27.4	23.8	20.3	5.1	1.1	0.0
7	28.7	25.0	21.5	5.3	1.2	trace
8	29.6	26.0	22.5	5.5	1.3	trace
9	30.4	26.8	23.2	5.6	1.4	trace
10	31.2	27.6	23.8	5.6	1.4	trace

Effect of Neutralization of Normal NaOH after 15-Minute Contact.

Time after adding H_2O_2. (Minutes.)	0 cc.	0.1 cc.	0.2 cc.	0 4 cc.	0 6 cc.	0 8 cc.
1	9.4	5.6	5.4	0.7	0.0	0.0
2	15.8	10.6	10.6	1.9	trace	0.0
3	20.2	14.4	14.3	2.4	0.2	0.0
4	23.5	17.5	16.9	2.7	0.4	0.0
5	25.7	19.8	17.3	2.9	0.5	0.0
6	27.4	21.6	18.4	3.2	0.7	0.0
7	28.7	23.0	19.3	3.2	0.8	0.0
8	29.6	24.1	19.9	3.3	0.8	0.0
9	30.4	25.0	20.3	3.4	0.9	0.0
10	31.2	25.7	20.8	3.5	0.9	0.0

TABLE XI.

Effect of 15-Minute Contact with Normal NH_4OH.

Time after adding H_2O_2. (Minutes.)	Normal NH_4OH added.					
	0 cc.	0.2 cc.	0.4 cc.	0.8 cc.	5 cc.	10 cc.
			Oxygen developed.			
1	8.8	6.3	6.4	6.1	4.9	3.2
2	14.4	12.3	12.6	12.3	9.5	7.4
3	18.7	16.4	17.2	17.1	13.3	11.6
4	21.6	20.0	20.6	20.8	16.1	15.0
5	24.3	22.5	23.2	23.2	18.4	17.8
6	26.3	24.5	25.3	25.0	20.1	20.1
7	27.8	26.2	26.9	26.4	21.6	22.0
8	29.4	27.3	28.1	27.6	22.8	23.4
9	30.7	28.6	29.1	28.5	24.0	24.7
10	31.4	31.1	30.0	29.3	24.8	25.9
Effect of Neutralization of NH_4OH after 15-Minute Contact.						
1	8.8	4.1	2.4	1.0	0.0	trace
2	14.4	8.5	5.9	3.2	trace	trace
3	18.7	12.3	8.9	5.2	0.2	trace
4	21.6	15.4	11.3	6.6	0.2	trace
5	24.3	18.0	13.9	7.9	0.2	trace
6	26.3	20.1	15.8	9.0	0.2	trace
7	27.8	21.7	17.4	10.1	0.2	trace
8	29.4	23.0	18.5	10.9	0.3	trace
9	30.7	24.1	19.9	11.6	0.3	trace
10	31.4	25.1	20.3	12.2	0.3	trace

TABLE XII.

Effect of 15-Minute Contact with Normal Na_2CO_3.

Time after adding H_2O_2. (Minutes.)	Normal Na_2CO_3 added.				
	0 cc.	0.1 cc.	0.2 cc.	0.4 cc.	0.8 cc.
			Oxygen developed.		
1	9.0	7.2	7.7	6.4	6.4
2	15.7	13.1	13.6	12.3	12.3
3	20.0	17.2	17.8	16.5	16.3
4	23.3	20.4	20.8	19.7	19.5
5	26.2	23.0	23.0	22.3	21.7
6	28.3	25.0	24.7	24.2	23.6
7	30.2	26.5	26.3	25.7	25.0
8	31.6	27.8	27.5	26.9	26.3
9	32.7	28.8	28.4	28.0	27.2
10	33.6	29.7	29.4	28.8	28.1
Effect of Neutralization of Normal Na_2CO_3 after 15-Minute Contact.					
1	9.0	6.6	5.7	4.5	4.5
2	15.7	12.7	10.6	8.9	8.1
3	20.0	15.8	14.3	12.4	10.6
4	23.3	18.9	17.3	14.9	12.7
5	26.2	21.3	19.7	17.0	14.2
6	28.3	23.3	21.6	18.6	15.6
7	30.2	25.0	23.1	20.0	16.6
8	31.6	26.2	24.4	21.0	17.4
9	32.7	27.3	25.5	21.9	18.1
10	33.6	28.1	26.2	22.6	18.6

acids was not studied but it is quite probable that the same observations would hold true, as all show a much less inhibiting action toward catalase.

Having shown the effect of some of the more important inorganic and organic acids toward the catalase of taka-diastase, we next tried the effect of alkalies. The methods used in this work were the same as those employed in the previous experiments. The effect of various concentrations of alkalies on the enzyme solution was studied, and a parallel experiment was also performed with each alkali included in this series to show the effect of exactly neutralizing the alkali with standard hydrochloric acid after fifteen-minute contact of enzyme with alkali. The results are expressed in the preceding tables.

In addition to the results given in the preceding tables for sodium carbonate, tests were made with much stronger concentrations of the alkali. The maximum concentration used was 5 cc. of twice normal sodium carbonate. In no instance was it possible to effect a lowering of the enzyme activity beyond the point given in the table for 0.8 cc. concentration. Neutralization of the alkali with acid showed a decided decrease in activity. Additional concentrations of alkali, besides those given in the table, were not tried with potassium carbonate and acid sodium carbonate.

TABLE XIII.

Effect of 15-Minute Contact with Normal K_2CO_3

Time after adding H_2O_2. (Minutes)	Normal K_2CO_3 added 0 cc	 0.1 cc	 0.2 cc	 0.4 cc	 0.8 cc
			Oxygen developed.		
1	8.3	7.7	7.0	6.6	6.3
2	15.0	14.1	13.2	12.6	12.6
3	19.4	19.3	18.5	17.2	17.0
4	23.2	22.8	22.1	20.6	20.2
5	26.2	25.9	24.6	23.6	23.6
6	28.3	27.4	26.3	25.6	24.3
7	30.0	28.7	27.9	27.2	25.7
8	31.3	29.8	29.0	28.0	27.0
9	32.3	30.6	29.6	28.9	27.9
10	33.2	31.3	30.7	29.8	28.7
Effect of Neutralization of Normal K_2CO_3 after 15-Minute Contact.					
1	8.3	6.0	5.7	5.8	4.1
2	15.0	11.8	10.6	10.0	7.2
3	19.4	16.4	15.0	13.4	9.7
4	23.2	19.9	18.2	16.2	11.7
5	26.2	22.7	20.6	18.5	13.2
6	28.3	24.7	22.7	20.2	14.4
7	30.0	26.3	24.1	21.7	15.2
8	31.3	27.7	25.5	22.9	15.9
9	32.3	28.8	26.6	23.9	16.5
10	33.2	29.7	27.4	24.6	17.0

TABLE XIV.

Effect of 15-Minute Contact with Normal $NaHCO_3$.

Time after adding H_2O_2. (Minutes.)	Normal $NaHCO_3$ added.				
	0 cc.	0.1 cc.	0.2 cc.	0.4 cc.	0.8 cc.
	Oxygen developed.				
1	7.2	6.3	6.1	6.1	5.6
2	13.4	11.9	11.7	11.7	11.2
3	18.2	16.6	16.2	16.1	15.5
4	21.9	20.2	19.6	19.6	18.9
5	24.8	23.3	22.5	22.3	21.7
6	27.1	25.4	24.7	24.6	23.9
7	29.0	27.3	26.6	26.4	25.7
8	30.5	28.7	28.0	27.9	27.2
9	31.5	29.8	29.1	28.9	28.4
10	32.6	30.7	30.1	29.9	29.3
Effect of Neutralization of Normal $NaHCO_3$ after 15-Minute Contact.					
1	7.2	5.4	4.8	4.3	1.7
2	13.4	11.1	10.0	8.9	4.2
3	18.2	15.6	14.1	12.3	6.7
4	21.9	19.2	17.4	15.2	8.8
5	24.8	21.9	20.1	17.6	10.5
6	27.1	24.1	22.0	19.5	11.9
7	29.0	25.7	23.7	21.0	13.0
8	30.5	27.1	25.1	22.1	13.8
9	31.5	28.2	26.2	23.3	14.5
10	32.6	29.1	27.2	24.1	15.1

The preceding work shows the relative inhibiting effect of bases when in contact with the enzyme solution for fifteen minutes. The following tables show the inhibiting effect of 0.4 cc. normal NaOH and KOH on the taka-diastase solution when allowed to remain in contact for different periods of time:

TABLE XV.

Effect of 0.4 cc. Normal NaOH for Different Periods of Contact.

Time after adding H_2O_2. (Minutes.)	Control.	0.4 cc. normal NaOH added. Time of contact in minutes.			
		0.	15.	30.	60.
		Oxygen developed			
1	6.8	4.5	2.0	1.9	0.7
2	13.1	9.2	3.9	3.8	1.7
3	18.0	10.5	5.6	5.2	2.4
4	21.6	16.2	6.8	6.4	3.0
5	24.5	18.5	7.9	7.3	3.4
6	26.6	20.1	8.7	8.0	3.8
7	28.2	21.4	9.3	8.5	4.0
8	29.8	22.4	9.8	8.9	4.2
9	30.8	23.1	10.1	9.2	4.4
10	31.8	23.8	10.4	9.4	4.5

The action of bases toward catalase is somewhat similar to the action of acids. Sodium and potassium hydroxide are nearly equal in their effect and they show a much stronger reduction of the activity than the remain-

TABLE XVI.

Effect of 0.4 cc. Normal KOH for Different Periods of Contact.

Time after adding H_2O_2. (Minutes)	Control.	0.4 cc. normal KOH added Time of contact in minutes. 0	15	30	60
		Oxygen developed			
1	7.9	2.9	1.4	1.0	0.3
2	14.1	6.1	2.9	1.8	1.0
3	18.5	9.3	4.1	2.7	1.4
4	21.8	11.8	5.2	3.9	1.8
5	24.5	13.7	6.0	4.1	2.0
6	26.7	15.3	6.7	4.6	2.2
7	29.3	16.4	7.2	5.1	2.4
8	29.8	17.6	7.5	5.3	2.5
9	30.9	18.3	7.7	5.6	2.6
10	31.8	18.8	8.0	5.7	2.7

ing alkalies. Ammonium hydroxide, potassium carbonate, sodium carbonate and sodium bicarbonate show only a slight depressing effect. It is a noticeable fact that neutralization of the alkali by a standard solution of hydrochloric acid increases the retarding effect in every instance.

The duration of contact with sodium and potassium hydroxide has a decided effect upon the enzyme activity. The results show a lowering of enzyme activity when the time of contact is increased.

The results obtained with catalase preparations from different sources, however, are hardly comparable, as it is only reasonable to suppose that the purity of the catalase solutions materially affects the results.

Summary.

I. The inhibiting effect of acids and alkalies upon the catalase of taka-diastase follows the order of their ionization constants.

II. After fifteen-minute contact with acid or alkali, the activity of the enzyme cannot be restored by neutralization.

III. The effect of acids was not influenced by the time of contact within the limits of these experiments. The effect of caustic alkalies, on the other hand, was proportional to the period of contact.

In conclusion, the writer takes pleasure in acknowledging his indebtedness to A. W. Dox for his kind suggestions in carrying out this work.

AMES, IOWA.

[CONTRIBUTION FROM THE HAWAII EXPERIMENT STATION NO. 11.]

THE ORGANIC NITROGEN OF HAWAIIAN SOILS. I. THE PRODUCTS OF ACID HYDROLYSIS.

BY W. P KELLEY

Received November 10, 1913.

Introduction.

The vegetable proteins occurring in different plants constitute the principal source of the soil nitrogen. These undergo biological decompositions of a hydrolytic nature, which probably take place in a gradational manner similar to that which occurs during animal digestion. The chemistry of soil nitrogen, therefore, may be looked upon as being the chemistry of protein undergoing hydrolysis.

For some time it has been the practice among soil bacteriologists to determine the ammonia split off by bacterial action and the rates of its oxidation to nitrate under varying conditions. But ammonia is the final hydrolytic product and is probably split off, in the main, directly from the acid amides and amino acids which have themselves arisen from hydrolysis of the proteins. Hence, the determination of the organic nitrogen compounds that are obtainable from a soil, ought to throw some light on the possibilities of subsequent ammonification, and indicate the nature of the decompositions that have already taken place. This view of the subject receives support from the recent researches of Jodidi[1] who found that different acid amides and amino acids undergo ammonification in soils at different rates, depending upon their structure. He found, for example, that glycocoll and leucine were ammonified more rapidly than phenylalanine, which he attributes to the resistant character of the benzene ring occurring in the last named compound.

The vegetable proteins, upon hydrolysis, yield amide, basic and non-basic nitrogen in quite variable amounts, as shown by Osborne.[2] The amide nitrogen ranges from 6% in legumelin from the horse bean to 24.5% in gliadin from wheat. The basic nitrogen varies from 3% in zein from maize to 32.8% in globulin from the cocoanut; while the non-basic nitrogen occurs in more constant and always much larger amounts. The average of the 34 different vegetable proteins reported contain 11.6% amide, 23.6% basic and 63.5% non-basic nitrogen.

It is evident, then, that soil organic matter originating from different plants would probably yield, upon hydrolysis, varying amounts of amide, basic and non-basic nitrogen compounds. During recent years some investigation has been made on this subject. From the researches of Shorey,[3] Jodidi,[4] Robinson[5] and Lathrop, and Brown,[6] it has been shown that the acid soluble nitrogen of soils varies considerably. On the average, the hydrolytic products have been found to be composed of approximately 25% amide, 10% basic and 65% non-basic nitrogen.

Schreiner,[7] Shorey and their associates in the Bureau of Soils have isolated a number of nitrogen compounds from soils, the specific nature

[1] Iowa Sta., *Research Bull.* 9 (1912).

[2] The vegetable proteins.

[3] U. S. D. A., Hawaii Sta., *Ann. Rept.* 1906, 37–59.

[4] Mich. Sta., *Tech. Bull.* 4 (1909); Iowa Sta., *Research Bulls.* 1 and 3 (1911).

[5] Mich. Sta., *Tech. Bull.* 7 (1911).

[6] *J. Ind. Eng. Chem.*, 3, 657–60 (1911).

[7] U. S. D. A., Bur. of Soils, *Bulls.* 47, 53, 74, 80, 87, 88, 89.

of which indicates that the biological decompositions going on produce cleavages analogous to those brought about upon acid hydrolysis of the proteins.

In view of the limited number of soils previously studied in this connection, and the strong probability that under bacterial action hydrolysis of the proteins takes place previous to the deamidization process proper, it is desirable that a greater range of soils be investigated with reference to their nitrogen constituents.

The Nitrogen of Hawaiian Soils.

The soils used in this investigation belong to the laterite class common to the islands. Sample No. 379 is a silty loam, containing considerable amounts of organic matter, and was taken from an old pasture where semi-arid conditions prevail.

Sample No. 428 is a highly organic sandy soil, recently cleared of a tropical jungle, and may be considered virgin fern forest land.

Sample No. 446 is a silty loam now being used for pineapples, but formerly devoted to pasture for many years.

Sample No. 292 represents a loam soil containing considerable gravel, and has been devoted to aquatic agriculture for many years.

Samples Nos. 343, 405, 406 and 345 are silty soils, and No. 347 is a highly humous soil, each of which have been continuously cultivated in rice for thirty or more years.

Nitrate and Ammonia.—Nitrates and ammonia, generally comprising not more than a small percentage of the total nitrogen in soils, were determined as follows: Nitrate was determined in water solutions, by the use of the phenol-disulfonic acid method, while the ammonia was determined by the direct distillation of separate portions of the soil after adding magnesium oxide. All the data presented in this paper have been calculated to the water-free basis.

TOTAL, NITRATE AND AMMONIA NITROGEN.

Total nitrogen.		Nitrate nitrogen		Ammonia nitrogen	
Lab. No.	Per cent.	Pts per million	Per cent. of total nitrogen	Pts per million	Per cent of total nitrogen
379	0.592	10	0.169	10	0.169
428	0.770	45	0.519	220	2.857
447	0.354	62	0.751	10	0.282
292	0.122	4	0.328	10	0.819
343	0.220	0	0.000	22	1.000
345	0.218	0	0.000	32	1.468
347	1.241	70	0.537	130	1.048
405	0.195	1	0.049	50	2.564
406	0.456	15	0.325	60	1.316

It will be observed that in contrast to soils elsewhere the ammonia content in most instances was found to be considerably greater than the nitrate,[1] and the nitrogen present as nitrate and ammonia constitutes only a small precentage of the total nitrogen. The nitrogen of these soils, as was expected, exists, therefore, very largely in organic combinations.

The Organic Nitrogen.—In this work the Osborne-Harris[2] modification of the Hausmann[3] method, as outlined by Jodidi[4] in his studies on Iowa soils, has been used. The hydrolysis was conducted by heating to boiling under a reflux condenser for 10 hours, 50 gram portions of the air-dried soils with 750 cc. strong hydrochloric acid, filtering and making the filtrate to one liter. Aliquot parts of the solution thus obtained were used for the determination of the amide, basic, and non-basic nitrogen. Since the amide nitrogen was determined as ammonia by the direct distillation of the solution after making alkaline with magnesium oxide, the ammonia originally present in the soil was deducted from the amounts found.

The basic nitrogen was determined by precipitation with phosphotungstic acid in water solutions, obtained by filtering the residue left after the distillation with magnesium oxide, and, as shown by previous investigators,[5] this precipitate contains nitrogen largely in the form of diamino acids, although it should be remembered that alkaloids, etc., if present, would also be precipitated. The non-basic nitrogen was determined by subtracting the sum of the other two groups from the total nitrogen dissolved, and while this group is now commonly referred to as mono-amino acids, Jodidi and Robinson have each brought forth evidence that it is not made up wholly of mono-amino acids. Just what other bodies occur in this group is not yet known. The results follow

ORGANIC NITROGEN OF HAWAIIAN SOILS

Soluble in Hydrochloric Acid.

Lab No	Per cent of total N.	Per cent. of the soil.				Per cent of nitrogen in solution.		
		Amide N	Basic N.	Non-basic N	Total N	Amide N	Basic N	Non-basic N.
379	71.96	0.095	0.030	0.300	0.426	22.30	7.04	70.42
428	72.59	0.141	0.028	0.368	0.559	24.79	5.01	66.27
447	67.51	0.074	0.033	0.131	0.239	30.96	13.81	54.82
292	91.80	0.024	0.012	0.075	0.112	21.43	10.71	66.96
343	90.91	0.054	0.020	0.124	0.200	27.00	10.00	62.00
345	88.52	0.042	0.017	0.131	0.193	21.76	8.81	67.88
347	80.42	0.225	0.097	0.663	0.998	22.55	9.72	66.43
405	84.62	0.042	0.019	0.099	0.165	25.45	11.51	60.00
406	91.22	0.079	0.055	0.276	0.416	18.99	13.22	66.35
					Av.	23.91	9.98	64.57

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[1] The occurrence of large quantities of ammonium compounds is a phenomenon common to many Hawaiian soils and will be further discussed in a separate publication.

[2] THIS JOURNAL, 25, 323 (1903).

[3] *Z. physiol. Chem.*, 27, 95 (1899).

[4] Iowa Sta., *Research Bull.* 1 (1911).

[5] Jodidi, *loc. cit.*; Robinson, *Ibid.*

It will be seen from the above table that there is considerable variation in the amounts of nitrogen dissolved from the different soils. In soil No. 447 only 67.51% of the total nitrogen was dissolved, while No. 292 yielded 91.80%. Concerning the insoluble nitrogen very little indeed is known.

Amides.—The amide nitrogen in all the soils studied, with the exception of Nos. 447, 343 and 406 occurred in approximately the same relative amounts, being on the average 23.91% of the soluble nitrogen. It is noteworthy that the amides of soils comprise a considerably higher percentage of the nitrogen than occur in most of the vegetable proteins previously studied. A direct comparison of the amide nitrogen of the above soils with that found in soils elsewhere is possible in a few cases only, for the reason that the strengths of the acid, and the lengths of the time of digestion, used in the investigations on this subject vary too greatly. With the results obtained by Jodidi, however, these data are comparable, and show that Hawaiian soils contain approximately the same relative amounts of amide as Michigan peat and Iowa soils.

Basic Nitrogen.—The nitrogen compounds precipitated by phosphotungstic acid were found to vary considerably in the different soils, amounting on the average to 9.98% of the soluble nitrogen. It is noteworthy that the percentage of basic nitrogen in soils falls far below the percentage found in the majority of vegetable proteins. In these studies no attempt was made to prove the nature of these nitrogen compounds, but from the work of others it seems permissible to consider the basic nitrogen as being composed principally of diamino acids.

Non-basic Nitrogen.—The percentages of non-basic nitrogen, with the exception of that from soil No. 447, were found to be remarkably similar in every instance, amounting to about two-thirds of the nitrogen dissolved by boiling hydrochloric acid. In this respect the soluble nitrogen of soils is quite similar to that of vegetable proteins. The non-basic nitrogen of soils as stated above is looked upon as being composed largely, but not entirely, of mono-amino acids, and probably such as are obtained in the hydrolysis of protein. Robinson,[1] for example, isolated leucine and isoleucine from hydrochloric acid solutions of Michigan peat.

Discussion.

As shown above, the relative amounts of amide nitrogen split off from the soils studied was about double that previously found in the seed proteins, while less than one-third as much basic nitrogen was found. On the other hand, the relative amounts of non-basic nitrogen proved to be about equal to that of the seed proteins. These variations may be due to the bacteria's attacking protein more largely at certain points than others, resulting in the splitting off of relatively greater amounts of basic nitrogen compounds than of the other groups,[1] and the basic nitrogen compounds then becoming diamidized, thus materially reducing the amounts of basic nitrogen present.

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[1] *Loc. cit.*

It is also possible for certain diamino acids to become transformed into diamines, as for example, arginine can be decomposed into urea and ornithine, then into putrescine, while lysine can be converted into cadaverine by the action of certain putrefactive bacteria. The urea that would thus be formed is known to be susceptible to the attack of a specific group of bacteria which convert it into ammonium compounds.

These views should not be interpreted to mean that bacteria attack protein at the diamino linkings only; there is much evidence that hydrolysis also takes place all along the line, resulting in the cleavage of amide, diamino and mono-amino acid compounds, all of which doubtless undergo ammonification, although probably at different rates.[2]

It should also be remembered that certain organic nitrogen compounds are readily assimilated by plants, others to a less extent, while still others are incapable of being assimilated.[3] Therefore, it is possible that the nitrogen compounds belonging to one group may be absorbed by plants to a greater extent than those of other groups. In view of these facts it is apparent that an explanation of the striking differences found in the percentages of nitrogen split off in the different groups in soils, on the one hand, and vegetable proteins, on the other, can only be surmised at the present time. Further investigation on this subject will be undertaken.

HONOLULU, HAWAII.

[CONTRIBUTION FROM THE HAWAII EXPERIMENT STATION NO 13]

THE ORGANIC NITROGEN OF HAWAIIAN SOILS. II. THE EFFECTS OF HEAT ON SOIL NITROGEN.

BY W. P. KELLEY.

Received November 10, 1913.

Introduction.

It has been observed frequently that soil heating produces notable effects on the growth of crops. With the exception of the studies carried out in the Bureau of Soils, the investigations on this subject have dealt largely with bacteriological and physiological phases of the question. In this connection, Lyon and Bizzel[4] observed that an increase in the solubility of the organic matter and the amounts of ammonia was produced by steam heating.

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[1] Since this paper was written results have been obtained from ammonification experiments, employing different nitrogenous materials, which strengthen the view that the basic nitrogen group is eliminated from soils at a greater rate than the amide and non-basic nitrogen compounds.

[2] See Jodidi, Iowa Sta., *Research Bull.* 9 (1912).

[3] See Hutchinson and Miller, *Jour. Agr. Sci.*, 4, 262–89; also, Schreiner and Skinner, U. S. D. A., Bur. of Soils, *Bull.* 77.

[4] Cornell Sta., *Bulls.* 275 and 326.

Lathrop and Brown[1] have shown in a study of the soils from the Pennsylvania Experiment Station, that steam heating under pressure brought about increases in the solubility of the nitrogen and the amounts of ammonia present, which increases were roughly proportional to the pressures used.

Schreiner and Lathrop[2] have shown, from an investigation of two different soils, that a number of organic compounds are split off by steam heating under pressure. It is of interest that all but two of the nitrogen compounds isolated are decomposition products of nucleo-protein. Moreover, certain differences were observed in the nitrogen compounds occurring before heating, although each soil had previously been treated with the same kinds of organic manures; still other compounds occurred only after heating. Of these guanine and arginine were split off from one soil, while adenine was split off from the other.

The Effects of Heat on Hawaiian Soils.

In connection with investigations on the organic nitrogen of Hawaiian soils, some study has been made on the effects produced by heat.

Nitrate and Ammonia.—A number of soils representing different types common to Hawaii were subjected to definite temperatures by heating 100 gram portions in procelain dishes in an air bath for two hours. Steam heat at two atmospheres pressure was also applied. The nitrates were determined by the phenol-sulfonic acid method, and ammonia by direct distillation after adding magnesium oxide. It should be remembered that a portion of the ammonia thus obtained probably occurred in the soils, especially after heating, as amides, rather than ammonium compounds, but, in view of the difficulties in separating amide from ammonia nitrogen in soils, the data will be referred to in this paper as ammonia.

Of the soils studied, No. 9 is a silty soil, containing large amounts of manganese dioxide; No. 290 is a heavy clay soil; Nos. 292 and 407 are clay loams containing considerable gravel; No. 335 is composed very largely of coral sand ($CaCO_3$) with only small amounts of organic matter; and No. 411 is a silty soil containing large amounts of humus.

The data below show that the nitrates of soils undergo decomposition with heating, gradually disappearing as the temperature increases. At 100° only slight decomposition took place; at 150° considerable decomposition was produced; while heating to 200° caused almost complete decomposition of nitrate. Steam heating at a pressure of two atmospheres produced effects similar to those that took place from heating to 150° without pressure.

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[1] *J. Ind. Eng. Chem.*, 3, 657–60 (1911).

[2] U. S. D. A., Bur. of Soils, *Bull.* 89 (1912).

The Effects of Heat on the Nitrate and Ammonia Content of Soils.

(Expressed in Percentages of Total Nitrogen.)

Temperature.	Soil No. 9.	Soil No. 290.	Soil No. 292.	Soil No. 335.	Soil No. 407.	Soil No. 411.
	Nitrate Nitrogen.					
Unheated	2.89	0.95	1.17	0.21	0.02	1.02
100°	2.54	0.98	0.87	0.12	0.02	1.09
150°	1.53	0.66	1.56	0.19	0.01	0.03
200°	0.13	0.34	0.23	0.04	0.01	0.03
250°	0.14	0.03	0.09	0.06	0.01	0.01
Steam, 2 atmospheres pressure	2.52	0.55	0.83	0.06	0.02	0.87
	Ammonia Nitrogen.					
Unheated	0.75	0.95	0.75	0.79	0.22	0.36
100°	0.64	1.03	0.70	1.14	0.33	0.51
150°	1.80	2.43	2.15	1.09	0.70	1.41
200°	5.03	24.46	11.62	2.14	8.98	3.11
250°	1.09	10.87	22.40	1.22	2.80	1.78
Steam, 2 atmospheres pressure	2.23	2.69	1.12	1.01	1.13	1.26

Heating to 100° produced but little effect on the ammonia content. At 150° considerable increases in ammonia were observed, and in passing from 150° to 200° very large increases took place, followed, in every instance except one, by notable decreases at 250°. The falling off in the ammonia content at the higher temperature was no doubt due to the expulsion of the products of decomposition from the soil mass. Steam heating at two atmospheres' pressure split off practically the same amounts of ammonia as dry heat at 150° without pressure. The nitrogen compounds of soils, therefore, undergo decomposition with heating, and among the products formed those which yield ammonia upon distillation with magnesium oxide are produced in notable amounts.

The organic nitrogen groups, both before and after heating, were determined by the use of the method of acid hydrolysis as outlined in the previous paper. In this way it was hoped to determine the effects produced on the different groups of nitrogen compounds, and indirectly throw some light on the nature of bacterial action in soils. Since heating to 200° led to the greatest accumulation of ammonia, this temperature was employed. The data obtained from five different soils are submitted in the following table.[1]

Considering first the soils before heating, it will be seen that the percentage of the different groups of nitrogen bodies dissolved by hydrochloric acid varied considerably. Expressing these results in percentages of the total nitrogen dissolved, the non-basic nitrogen on the average equalled 63.82%, the amide 24.21%, and the basic nitrogen 10.13%. The ammonia was determined previous to treating with hydrochloric acid, and by calculation was found to equal 1.81% of the nitrogen dissolved.

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[1] The data submitted in this table vary slightly from those recorded in the previous paper, and bearing the same lab. no. This is due to different samples of the same soil having been used.

EFFECTS OF HEAT ON THE NITROGEN OF HAWAIIAN SOILS.

				Soluble in hydrochloric acid								
				Per cent of soil			Total		Per cent of nitrogen in solution			
Lab No.	Total N Per cent of soil	Nitrate N Per cent of soil	Ammonia N Per cent of soil	Amide nitrogen	Basic nitrogen	Non-basic nitrogen	Per cent of soil	Per cent of total nitrogen	Ammonia nitrogen	Amide nitrogen	Basic nitrogen	Non basic nitrogen
Before Heating												
379	0 546	0 001	0 001	0 096	0 030	0 299	0 426	78 02	0 23	22 53	7 04	70 18
428	0 779	0 005	0 022	0 129	0 029	0 378	0 558	71 63	3 94	23 12	5 09	67 74
447	0 396	0 006	0 001	0 074	0 033	0 131	0 239	60 35	0 41	30 96	13 81	54 82
405	0 179	Trace	0 005	0 042	0 019	0 099	0 165	92 18	3 03	25 45	11 51	60 00
406	0 504	0 002	0 006	0 079	0 055	0 276	0 416	82 54	1 44	18 99	13 22	66 35
Av	0 481	0 003	0 007	0 084	0 033	0 237	0 361	76 94	1 81	24 21	10 13	63 82
After Heating (200°)												
379	0 417	0 0	0 069	0 098	0 034	0 168	0 369	88 49	18 69	26 56	9 21	45 53
428	0 608	0 0	0 031	0 077	0 023	0 079	0 210	34 54	14 76	36 66	10 95	37 62
447	0 207	0 0	0 020	0 039	0 022	0 028	0 109	52 66	18 35	35 78	10 18	25 69
405	0 178	0 0	0 036	0 056	0 019	0 041	0 152	85 39	23 68	36 84	12 50	26 97
406	0 419	0 0	0 067	0 103	0 019	0 092	0 281	67 06	23 84	35 65	6 76	32 74
Av	0 366	0 0	0 045	0 075	0 023	0 082	0 224	65 63	19 86	34 50	11 92	33 71

Upon heating notable changes took place; the ammonia increased from 0.007% to 0.045% of the moisture free soil, or from 1.81% to 19.86% of the nitrogen dissolved. The amounts of amide nitrogen in soils 428 and 447 were considerably reduced by heating, while those of soils 405 and 406 were slightly increased. In no instance, save soil No. 406, was there any notable change in the amount of basic nitrogen. On the average then, heat effected but little change in the amounts of amide and basic nitrogen present. Considering the non-basic nitrogen, on the other hand, notable losses were sustained from the heating.

The loss of nitrogen amounted, on the average, to approximately 25%, but in this respect considerable difference was observed in the different soils. Soil No. 447 suffered the heaviest loss, amounting almost to 50%, while the loss from No. 405 was within the limits of experimental error. Heating to 200° for two hours, therefore, caused a loss of nitrogen and the formation of large amounts of ammonia, which nitrogen came largely from the complexes that yield non-basic nitrogen upon acid hydrolysis.

In the previous paper some of the striking differences between soil nitrogen and that of the vegetable proteins were pointed out. It was shown, for example, that the nitrogen bodies split off from soil organic matter by boiling hydrochloric acid were made up of relatively greater amounts of amide, and correspondingly smaller amounts of basic nitrogen, than occur in the vegetable proteins. To account for this it was suggested that bacterial action probably causes a more marked splitting off of the basic nitrogen constituents, than of the other groups, at least in the early stages of the decomposition.

On the other hand it is shown in the present paper, that heat causes a breaking up of the organic nitrogen bodies in such a way as to liberate large amounts of ammonia from the antecedents of the non-basic nitrogen bodies—presumbaly the mono-amino acids.

HONOLULU, HAWAII.

THE ORGANIC NITROGEN OF HAWAIIAN SOILS.[1] III. THE NITROGEN OF HUMUS.

BY W. P. KELLEY AND ALICE R. THOMPSON.

Received December 15, 1913.

Introduction.

That part of the organic matter of soils soluble in dilute alkali, and known as humus, is generally considered to exert special influence on fertility. Moreover, it is claimed that the nitrogen contained in humus becomes available more readily than non-humus nitrogen. Dr. Hilgard found,[2] for instance, that during the first four months after extracting the humus from a soil, no nitrification took place, although the non-humus nitrogen in the soil amounted to 0.127%; after the lapse of two years' time an insignificant amount of nitrate was formed, whereas vigorous nitrification took place in the original soil. The fact that no nitrate was formed from the non-humus nitrogen until after several months' time, and then only at a very slow rate, suggests that the alkali-soluble nitrogen existed in different forms from the non-humus nitrogen. It should be borne in mind, however, that other factors than those having to do with the chemical nature of the nitrogen bodies also exert important influence on bacterial action, such factors as the food supply available to the bacteria, and the physical, chemical and biological conditions, all of which probably underwent some change as a result of extracting the humus.

The general interest taken in soil humus justifies some investigation on the nitrogen bodies contained. The so-called humification process has been the subject of much speculation for many years, but it must be admitted that very little definite knowledge exists regarding the chemistry involved in this process. Bacteria undoubtedly bring about manifold chemical changes in the organic matter, causing it to pass through varying degrees of decomposition leading up to the formation of humus, but regarding the transformations the nitrogen bodies undergo in this process little is known.

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[1] Contribution from the Hawaii Agricultural Experiment Station.

[2] *Soils*, pp. 358–60.

The experiments discussed below were undertaken with the view of learning something regarding the chemical nature of the nitrogen bodies contained in humus, and with the hope of gaining some light on the chemistry involved in the process. By comparing the different groups of nitrogen compounds in humus with those in the soil as a whole, it is conceivable that some suggestion might be obtained regarding the nature of the bacterial action that has previously taken place. The soils studied in this connection were the same as those employed in the investigations already reported from this laboratory.[1]

Nitrogen Soluble in 1 Per Cent. Hydrochloric Acid.

In order to break up combinations between the humus substances and inorganic matter and increase the solubility of the humus, the samples were treated in the cold with 1% hydrochloric acid until no further calcium and magnesium were dissolved, then filtered and washed free from acid with distilled water. The filtrates were evaporated to small volumes and analyzed. In a previous investigation carried out in this laboratory it was observed that the hydrochloric acid extracts thus obtained[2] contained, in some instances, considerable amounts of organic matter, and as shown by others,[3] considerable amounts of nitrogen may be dissolved in this way. In the following table are recorded the data showing the total nitrogen in the soils studied and the amounts dissolved by hydrochloric acid:

NITROGEN SOLUBLE IN 1% HCl.

		Soluble in HCl.	
Lab. No.	Total in soil. Per cent.	Per cent. of soil.	Per cent. of total N.
347	1.241	0 029	2.34
428	0.770	0.041	5.33
379	0.592	0 019	3 21
406	0.456	0.012	2.63
447	0.354	0.012	3.39
345	0.218	0 007	3.21
343	0 220	0 004	1.82
405	0.195	0 009	4.61
292	0.122	0.004	3 28
		Av.	3.31

Thus it is shown that small amounts of nitrogen were dissolved by 1% hydrochloric acid, and it is noteworthy that on the average these soils contained only about one-half as much nitrogen in the form of ammonia as was dissolved by hydrochloric acid.[4]

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[1] THIS JOURNAL; see preceding articles.

[2] U. S. D. A., Hawaii Sta., *Press Bull.* 33.

[3] Emery, THIS JOURNAL, 22, 285–91 (1900); Leavitt, *J. Ind. Eng. Chem.*, 4, 601–41 (1912).

[4] THIS JOURNAL, *loc. cit.*

The Humus Nitrogen.

Dilute ammonia is the solvent usually employed for dissolving humus, but it is apparent that humus solutions to be used in studies on the nitrogen bodies could not be made by the use of this solvent. For this purpose we have employed a 3% solution of sodium hydrate. Forty-gram portions of the air-dried soils, after having been extracted with dilute hydrochloric acid, were shaken with 2000 cc. of the sodium hydrate solution at intervals for one day, then allowed to settle for an additional day, after which, the solutions were siphoned off and aliquot portions used in the studies herein reported.

It is known that a part of the humus can be precipitated from alkali solutions by acids. The relative amounts precipitated, however, vary with the amounts of acid used. Shorey has shown,[1] for instance, that after filtering out the precipitate obtained by acidifying the solution, a still further precipitate was obtained by carefully neutralizing the filtrate, and that the precipitates thus obtained each contained nitrogen. In other words, humus nitrogen is soluble to some extent in water but more so in dilute hydrochloric acid.

In our work we have arbitrarily separated the humus into two portions by making neutral to litmus paper with hydrochloric acid 1000 cc. portions of the humus solutions (corresponding to 20 grams of soil), then acidifying by adding 20 cc. of 1% hydrochloric acid, filtering and washing the precipitate with dilute hydrochloric acid. The precipitates thus obtained were afterwards subjected to acid hydrolysis by boiling with 400 cc. strong hydrochloric acid for a period of ten hours, filtering and washing the residue. The amide and basic nitrogen were determined in the original humus solutions, in the filtrates obtained after filtering out the precipitates formed

THE NITROGEN OF HUMUS.

Lab. No.	Total per cent. of soil.	Precipitated by dilute HCl.		Not precipitated by dilute HCl. Per cent. of soil.	Total per cent. of soil. N.	Precipitated by HCl.		Not precipitated by HCl. Per cent. of humus N.
		Hydrolyzable per cent. of soil	Non-hydrolyzable per cent. of soil.			Hydrolyzable per cent. of humus N.	Non-hydrolyzable per cent. of humus N.	
347	0.774	0.362	0.125	0.315	62.37	45.14	15.59	39.28
428	0.590	0.289	0.051	0.247	76.62	49.23	8.69	42.08
379	0.439	0.270	0.041	0.129	74.16	61.36	9.32	29.32
406	0.226	0.100	0.027	0.117	49.56	40.98	11.06	47.96
447	0.215	0.094	0.026	0.105	60.79	41.78	11.56	46.67
345	0.147	0.066	0.019	0.070	67.43	42.58	12.26	45.16
343	0.127	0.061	0.012	0.069	57.73	42.96	8.45	48.59
405	0.123	0.044	0.012	0.067	63.08	35.77	9.76	54.47
292	0.058	0.031	0.012	0.015	47.54	53.45	20.69	25.86
				Average	62.15	45.92	11.93	42.15

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[1] U. S. D. A., Hawaii Sta., *Rep.* 1906, 51.

by acidifying the solutions and in the solutions obtained by hydrolyzing the precipitates formed.

In the preceding table are recorded the data showing the total nitrogen contained in the original humus solutions, and in the portions obtained by the different separations.

The above data show that the relative amount of humus nitrogen varied from soil to soil, having been found on the average to amount to 62.15% of the total nitrogen. In every instance, except two, more than one-half of the total nitrogen was dissolved by dilute alkali, while in two instances practically three-fourths of it was thus extracted. Likewise the bodies precipitated by dilute hydrochloric acid also contained nitrogen in varying amounts. The nitrogen bodies thus precipitated yielded by far the greater part of their nitrogen to the solution, the insoluble residue having been found to contain on the average 11.93% of the humus nitrogen. By these methods it is seen, therefore, that the nitrogen of humus can be separated into fractional parts.

Amide Nitrogen in Humus.

The amide nitrogen in the original humus solutions was determined as ammonia, after slightly acidifying with hydrochloric acid, by distillation with magnesium oxide. In similar manner the amide nitrogen was determined in the different portions of the humus. The results are shown in the following table:

AMIDE NITROGEN IN HUMUS.

Lab. No	Determined directly. Per cent of soil	Determined in filtrate after precipitation with dilute HCl. Per cent of soil (*a*).	Determined in precipitate after subjecting to acid hydrolysis. Per cent of soil (*b*)	Total.		
				a and *b*.	Per cent of total soil N.	Per cent. of total humus N.
347	0.100	0.095	0.073	0.168	13.54	21.70
428	0.073	0.074	0.056	0.130	16.88	22.03
379	0.059	0.056	0.061	0.117	19.76	26.65
406	0.039	0.040	0.020	0.060	13.15	26.55
447	0.033	0.031	0.027	0.058	16.38	26.98
345	0.025	0.022	0.016	0.038	17.43	25.85
343	0.020	0.025	0.018	0.043	19.54	33.86
405	0.026	0.014	0.023	0.037	18.97	42.53
292	0.009	0.008	0.011	0.019	15.57	32.76
				Average	16.80	28.77

The relatively high percentage of amide nitrogen contained in the original humus solutions is noteworthy. It is apparent that the amide compounds are soluble in dilute hydrochloric acid, as shown by the fact that the filtrates contain practically the same amount of amide as the original solutions. On the average the precipitates yielded upon hydrolysis practically the same amounts of amide nitrogen as were contained as such in the original solutions. The total amide nitrogen when calculated to percentages of the total soil nitrogen varies somewhat, but on the average amounted to 16.80%. When calculated to percentages of the humus nitrogen it will be seen that the amide nitrogen varied inversely with percentages of the humus nitrogen. On the average 28.77% of the humus nitrogen was found to be in the form of amide.

The percentage of amide nitrogen obtained by hydrolyzing these soils as a whole was previously shown to equal[1] 23.91% of the soluble nitrogen, and, while it is true that the absolute amounts of amide nitrogen in the humus amounted to somewhat less than that in the original soils, the percentages in the humus solutions when calculated to percentages of the humus nitrogen were greater.

Basic Nitrogen of Humus.

The basic nitrogen in humus was determined, after removing the amides, by the phosphotungstic acid method, as already outlined. The results are recorded in the following table:

BASIC NITROGEN IN HUMUS.

Lab. No.	Determined in original solutions. Per cent. of soil.	Determined in filtrate after precipitation with HCl (*a*). Per cent. of soil.	Determined in precipitate after subjecting to acid hydrolysis (*b*). Per cent. of soil.	Total (*a* and *b*).		
				Per cent. of soil.	Per cent. of total soil N.	Per cent. of total humus N.
347	0.028	0.024	0.010	0.034	2.74	4.39
428	0.027	0.025	0.010	0.035	4.81	5.93
379	0.017	0.021	0.007	0.028	4.73	6.38
406	0.015	0.014	0.009	0.023	5.05	10.18
447	0.021	0.019	0.006	0.025	7.06	11.63
345	0.003[2]	0.017	0.017	0.034	15.59[3]	23.13[3]
343	0.004[2]	0.017	0.008	0.025	11.36	19.68
405	0.011	0.009	0.008	0.017	8.71	19.54
292	0.014	0.009	0.017	0.026	21.31[3]	44.83[3]
				Average	6.35	11.10

The above data show that basic nitrogen occurred in practically the same amounts in both the original humus solutions and in the filtrates obtained by precipitation with dilute hydrochloric acid, indicating that the basic nitrogen compounds, present as such, are soluble in dilute acid, as was the case with the amides. It is also noteworthy that the precipitates contained less basic nitrogen than the filtrates. The total basic nitrogen, calculated to percentages of the total soil nitrogen, shows a tendency to increase with a decrease in the absolute amount of nitrogen present and when calculated to percentages of the total humus nitrogen the same relationships are borne out, but in a more marked degree.

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[1] *Loc. cit.*

[2] Too low, apparently due to error.

[3] Not included in average.

On the average, the amount of basic nitrogen in the humus solutions was somewhat less than was obtained by hydrolyzing the soil as a whole, whereas the percentage of basic nitrogen, when calculated to the basis of the humus nitrogen present, was considerably greater.

Non-basic Nitrogen.

It is obviously not permissible to consider the difference between the total nitrogen in humus, on the one hand and the amounts of amide and the basic nitrogen that occurred in the original humus solutions, on the other, as non-basic nitrogen, for the reason that these solutions cannot be considered to have been completely hydrolyzed. It is well known, for example, that various proteins are somewhat soluble in alkalies without the proteins undergoing any particular hydrolysis, as is shown by the fact that they can be precipitated in a more or less unaltered condition from such solutions. The nitrogen compounds in the filtrates obtained from precipitation with dilute hydrochloric acid, however, and also those split off in the hydrolysis of the humus precipitate, may reasonably be considered to be made up of amide, basic and non-basic nitrogen bodies. We have, therefore, calculated the amounts of non-basic nitrogen in these portions of humus. The results are shown in the following table:

NON-BASIC NITROGEN IN HUMUS.

			Total		
Lab No	In the filtrates after precipitation with HCl Per cent. of soil.	In the precipitates after subjecting to acid hydrolysis. Per cent of soil.	Per cent. of soil.	Per cent of total soil N	Per cent. of total humus N.
347	0.196	0.249	0 445	35 86	57.49
428	0.148	0.213	0 361	46 88	61.18
379	0.052	0.203	0 255	43 07	58.08
406	0.063	0.071	0 134	29 38	58 84
447	0.055	0.061	0.116	32 77	53 94
345	0.031	0.033	0.064	29.35	43.54
343	0.027	0.035	0.062	28 18	48 82
405	0.046	0 011	0 057	29 23	45 17
			Average	34.34	53 38

These data are of interest as showing the relatively large amounts of non-basic nitrogen in humus. It is especially noteworthy that on the average about 25% of the humus nitrogen occurred in the filtrates as non-basic nitrogen compounds, or 52.59% when calculated to percentage of the nitrogen soluble in dilute hydrochloric acid. Considering the solutions obtained upon hydrolyzing the humus precipitated by dilute hydrochloric acid, a still greater amount of non-basic nitrogen was found. On the average 64.84% of this nitrogen occurred in non-basic forms, which, when calculated to percentages of the total humus nitrogen, equals 31.98%. By combining these two portions it was found that 53.38% of the humus nitrogen was made up of non-basic nitrogen compounds. By referring to the data shown in the previous paper[1] it will be seen that the relative amounts of non-basic nitrogen in humus are somewhat less than the amounts obtained by hydrolyzing the soil as a whole.

Considering the different groups of nitrogen compounds obtained from humus, the preceding data show that in absolute amounts less amide, basic and non-basic nitrogen were contained in the humus than were split off upon hydrolysis of the soil as a whole. But on the other hand the humus nitrogen bodies, as such, contained relatively more amide and basic nitrogen and less non-basic nitrogen than the soil nitrogen as a whole. In other words, the nitrogen of soils soluble in 3% sodium hydrate is combined in bodies differing somewhat from the nitrogen bodies not soluble in the solvent.

While it cannot be definitely stated that no hydrolysis took place as a result of the treatments employed in the extraction of the humus and in the solutions subsequently, it seems probable that a considerable part of the humus nitrogen had already undergone some hydrolytic change in the soil. As previously stated, it is certain that the protein complex must become split up into simpler components before its nitrogen becomes available to plants. These components are now known to consist principally of acid amides and amino acids. The humification process, resulting in a considerable simplification of the protein complex with the probable cleavage of the amide, diamino and monoamino acids, therefore, is to be looked upon as a step towards the production of available nitrogen.

HONOLULU, H. I.

[FROM THE DEPARTMENT OF ANIMAL HUSBANDRY, UNIVERSITY OF ILLINOIS.]

A PRELIMINARY STUDY OF THE CHANGES OCCURRING IN MEATS DURING THE PROCESS OF DRYING BY HEAT AND IN VACUO.[2]

BY L. H. DAVIS AND A. D. EMMETT.

Received December 16, 1913.

It is a well known fact that some food products, when heated to 100–105°, give a lower percentage of dry substance, than when dried *in vacuo* at room temperature (20°), or lower.[1] Especially is this difference apparent for substances which contain certain sugars, oils, or fatty acids. On the other hand, there is a tendency for some of the fats to oxidize, when heated to 100–105°, and thus indirectly the dry substance of such materials is increased.

Of the two methods of drying, the use of heat at 100–105°, with or without a current of gas passing over the products, is generally used. It is simpler and can be carried out in a comparatively short time. In commercial work, the vacuum method is not practical, except in special cases where the heat method gives very erroneous results.

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[1] *Loc. cit.*

[2] The results presented in this paper formed part of the thesis which was submitted by Lloyd H. Davis to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Master of Arts in Chemistry.

In addition to the total loss or gain upon drying food materials at high temperatures, it is also of interest to study the chemical changes that take place during the process of drying *in vacuo* and some desiccating agent, as sulfuric acid, at room temperature. That is, to compare the composition of the fresh undried sample with the composition of a representative portion dried *in vacuo.*

The specific object of this investigation was, therefore, to procure information as to the comparative value of these two methods of drying with reference to meats. It involved: (1) a comparison of the dry substance and fat content of samples dried by the heat and vacuum methods; (2) a study of the influence of the resulting differences in the dry substance and the fat, upon the percentage values of the forms of nitrogen, and (3) a determination of the effect of vacuum drying upon the forms of nitrogen in the fresh undried meats.

Experimental.

Preparation of the Samples.—The meats were thoroughly ground and mixed. A portion of the fresh samples was analyzed immediately. The remainder of each sample of meat was desiccated as follows: It was spread out in thin layers over the bottom of Petri dishes. These vessels were then placed in a tight receptacle, which was in turn surrounded by a mixture of salt and ice. As soon as the meat was frozen, the dishes were transferred quickly to chilled vacuum desiccators which were then evacuated and put in a refrigerator. When the meat became dry enough to curl up around the edges, the dishes were carefully removed in order to turn the meat over and break it up. The sulfuric acid was also renewed at this time. The desiccators were again evacuated. The drying was then continued at room temperature (20°). After drying five or six days, the meat was taken out, and ground to pass through a millimeter sieve. The entire sample was again spread out in dishes and dried *in vacuo* at room temperature for two to three days. It was then mixed for analysis.

Determinations Made and the Methods Used.—The following constituents were determined in the fresh and desiccated meats: dry substance, fat, total nitrogen, water-soluble nitrogen, coagulable nitrogen, proteose nitrogen and creatin.

The methods used were as follows: 1. Dry substance by (*a*) the heat method and (*b*) the vacuum method.

(*a*) The weighed samples were dried at 100–105° in an air oven for 12 hours. They were then heated for periods of one and a half to two hours, until they became constant in weight.

(*b*) The samples were put in vacuum desiccators containing *pure* concentrated sulfuric acid. The desiccators were evacuated and placed upon an automatic shaker. The drying was continued for 4 to 5 days, the acid being renewed once during this time. The samples were then dried for 24-hour periods until they became constant in weight.

The dishes used in the drying were in all cases lead caps provided with closely fitted covers. The measurements of the dishes were $2^1/_4$ inches in diameter and $^3/_4$ inches deep. The caps and the corresponding covers were kept together and as soon as they were removed from the oven, in the case of the heat method, the covers were put over the caps at once and the whole placed in a desiccator. No more than six caps were put in the same desiccator. The weighings were made in about 45 minutes, after removing the dishes from the oven. In the case of the vaccum method, when the air was allowed to enter the desiccator in order to remove the dishes, it was dried by passing through sulfuric acid.

2. Fat. The dried residues, from 1*a* and 1*b* above, were extracted for at least 24 hours with dry redistilled ether. The fats were heated at 100–105° until they became constant in weight.

3. Total nitrogen. The Kjeldahl-Gunning-Arnold method was followed.[2] This involved the uses of mercury, potassium sulfate, and sulfuric acid. The digestion was continued for $2^1/_2$ hours after the charred mixture became clear.

4. Water-soluble nitrogen. In the case of the desiccated meats, the method of making the cold water extract was the same as the one which was formerly used in this laboratory.[3] For the fresh meats, a modification of this method was followed. This involved the use of a centrifuge and thoroughly extracted sand. The temperature of the water was about 10° in both cases.

5. The soluble nitrogen was determined by the same method as given in 3 above.

6. In the case of the coagulable nitrogen, aliquot portions of the water extract were evaporated to 30 cc., neutralized to litmus, heated again and filtered. The nitrogen was determined in the coagulum.

7. For the proteose nitrogen the filtrates from 6 were evaporated to 30 cc. After acidifying them with sulfuric acid, they were saturated with zinc sulfate. The nitrogen was then determined in the separated protein.

8. The creatin was estimated in portions of the water extract from which the coagula had been removed. Folin's method[4] as modified by Benedict and Myers, and by Emmett and Grindley was used.

Discussion of Results.

Effect of the Methods of Drying upon the Percentage of Dry Substance, Fat and Nitrogen.

The data for the dry substance and fat are given in Table I, calculated to the fresh basis. It will be seen, comparing the values for the heat and the vacuum methods, that there is a distinct difference between the percentage of dry substance in the two series of data. The vacuum method gives higher results in every case. This fact is more pronounced with the desiccated meats.

TABLE I.—THE PERCENTAGE OF DRY SUBSTANCE AND FAT IN THE FRESH AND DESICCATED MEATS

	Dry substance				Fat			
	Fresh meats		Desiccated meats		Fresh meats		Desiccated meats	
Lab No	Vacuum method	Heat method	Vacuum method	Heat method	Vacuum method	Heat method	Vacuum method	Heat method
312112	29 37	29 00	98 48	98 19	4 89	5 35	17 78	17 23
312512	26 83	26 69	99 05	97 18	3 79	3 90	15 64	15 62
313812	25 62	24 85	98 17	95 24	2 17	2 04	6 75	6 55
313912	25 89	24 97	98 51	97 25	1 62	1 54	4 99	4 76
313312	24 58[a]	lost	96 85	94 91	1 37[a]	lost	5 56[a]	4 32[a]
312612	24 40	23 95	[b]	[b]	2 02	2 07	[b]	[b]
313412	[b]	[b]	98 65	96 60	[b]	[b]	6 90	6 42
313512	[b]	[b]	96 71	95 35	[b]	[b]	9 64	9 68
Average	26 42	25 89	98 06	96 39	3 12	2 98	10 28	10 04

[a] Omitted from average
[b] Not determined

The average values are, for the fresh meats, 26.42 and 25.89% by the vacuum and heat methods, respectively, and for the desiccated meats, they are 98.06 and 96.39%. In the former case, there is a difference of 0.53% in favor of the vacuum method, and in the latter case, one of 1.67%. Expressed in per cent. of the total dry substance, determined by the vacuum method, the differences are 1.6 and 2.0% for the fresh and desiccated meats, respectively.

Comparing the data for the fat, there is no evidence as to whether the samples that were dried by the vacuum method gave higher, or lower, results than those that were dried by the heat method. With the exception of the one sample of the fresh meat, No. 312112, the differences are no greater than what one might expect to find between duplicate or triplicate determinations. Thus, the difference between the average values for the two series of data is 0.14% for the fresh meats, and 0.24% for the desiccated meats, while the average difference between duplicates by the heat method is 0.20, and by the vacuum method, 0.18%. The average results for the fat are for the fresh meats 3.12 and 2.98% for the vacuum and heat methods respectively, and for the desiccated meats, 10.28 and 10.04%.

In Table II, the data for the fat are calculated to the dry basis, using the two different values for dry substance. Excepting the sample of fresh meat No 312112, the differences between the two series of data cannot be attributed to the methods of drying, any more than to the errors that might have occurred in the sampling and the analysis. Taking the averages for the fresh meats, the values for the fat are 9.28 and 9.41% for the vacuum and heat methods, respectively, and in the desiccated meats, they are 10.44 and 10.36%.

TABLE II.—THE PERCENTAGE OF FAT IN THE FRESH AND DESICCATED MEATS.
Calculated to the Dry Basis.

	Fresh meats.		Desiccated meats.	
Lab. No.	Vacuum method.	Heat method.	Vacuum method.	Heat method.
312112	16.65	18.45	18.05	17.55
312512	14.13	14.61	15.79	16.07
313812	8.47	8.21	6.88	6.88
313912	6.26	6.17	5.07	4.89
313312	5.53	lost	5.74	4.55
312612	8.28	8.65	*a*	*a*
313412	*a*	*a*	6.99	6.65
313512	*a*	*a*	9.97	10.15
Average all, A	9.28*b*	9.41*b*	10.44*b*	10.33*b*
Average, B, 312112 to 312612	10.21	.	10.31	...

a Not determined.
b Omitted 313312.

From the above discussion of the data for the dry substance and fat, it would seem that the differences that occurred in the former constituent may be due to one or more of the following: (1) mechanical occlusion of water in the desiccated meats, or (2) loss of fatty matter in the subsequent heating of the fats extracted from the desiccated meats, or (3) the possible, although less probable, partial decomposition of the fresh meats by bacteria, during the early stages of the desiccation.

In order to show the influence of the two methods of drying upon the nitrogenous bodies in the meats, the results were calculated to the dry basis, using the two respective values. The averages are, for the fresh meats, 13.00% when vacuum dried, and 13.28% when heat dried, and for the desiccated meats, 13.50% and 13.74%, respectively. These differences are slight and as already stated for the dry substance, they amount to but 1.6 and 2.0%. They are no greater than those that were found to exist between the duplicate determinations.

To obtain more information as to the effect of heat upon the total nitrogen in meats, this constituent was determined in *triplicate* on representative portions of a sample of beef. Four portions were dried as follows: (*a*) 20 hours at 100–105°; (*b*) 96 hours at 100–105°; (*c*) until constant in weight *in vacuo* at room temperature (20°); and (*d*) 48 hours at 130°. The results, calculated to the fresh basis, are:

	Per cent. N.
(*a*) Dried at 100–105° for 20 hours	3.624
(*b*) Dried at 100–105° for 96 hours	3.615
(*c*) Dried *in vacuo* 20–25° to constant weight	3.632
(*d*) Dried at 130° for 48 hours	3 450

From these data, it would seem that there was but very slight loss, if any, on drying the meats at 100–105° as compared to the value found by the vacuum method. There was an apparent loss of nitrogen, however, upon raising the temperature to 130°.

Changes Occurring in the Forms of Nitrogen in Meats during Desiccation.

It has been shown in this laboratory that the composition of meats, when air-dried, compares very favorably with that of the fresh undried samples, when the two sets of data are calculated to the dry basis.[3] In these instances the analyses included dry substance by heat, fat, ash and total nitrogen.

TABLE III.—THE PERCENTAGE OF THE FORMS OF NITROGEN IN THE FRESH AND DESICCATED MEATS

			Water-soluble nitrogen.							
	Total nitrogen		Total		Coagulable.		Proteose		Creatin.	
Lab No	Fresh meats.	Desiccated meats	Fresh meats	Desiccated meats.	Fresh meats	Desiccated meats	Fresh meats	Desiccated meats.	Fresh meats	Desiccated meats.
312112	3.49	12 03	0 868	2 462	0 486	1 189	0 026	0 054	...	0 626
312512	3.42	12.30	0 746	2 372	0.386	0.788	0 028	0 181		...
313812	3.45	13 40	0 798	2 615	0.393	1.031	0.023	0 079	0 130	0.336
313912	3.51	13.99	0.717	2.535	0 374	1 209	0 014	0 061	0.115	0.503
313312	3 45	14 30	0 845	2 902	0 463	1 246	0.016	0 100		0.601

Referring to Tables I and III, the composition of the fresh and desiccated meats can be compared for corresponding samples, Nos. 312112 to 313312, inclusive. Owing to the higher per cent. of dry substance in the desiccated meats, their average composition differs greatly from that of the fresh samples. Therefore, a comparison of these data, calculated to the dry basis, will throw more light upon the question at issue.

In Table II, the data for the fat, calculated to the dry basis, show that the average percentage values are 10.21 and 10.31, respectively, for the fresh and desiccated meats. Comparing the results for the corresponding samples, the differences in fat are quite great in some cases. Thus, for sample No. 312112, the per cent. of fat in the fresh meat is 16.65, and in the desiccated meat 18.05. And in No. 313812, the percentage values are 8.47 and 6.88, respectively, for the undried and dried meats. There is no apparent explanation for this irregularity in the data.

The results for the nitrogen upon the dry basis are given in Table IV. The total nitrogen, with the exception of No. 312512 is higher in the desiccated meats. The average values are 13.14% for the fresh samples, and 13.45% for the desiccated samples. This difference is possibly the result of the reduction of some of the nitrogenous bodies, due to the action of bacteria in the early stages of the desiccation.

TABLE IV.—THE PERCENTAGE OF THE FORMS OF NITROGEN IN THE FRESH AND DESICCATED MEATS.

Results Calculated to the Dry Basis.

	Total nitrogen.		Water-soluble nitrogen.							
			Total		Coagulable.		Proteose.		Creatin.	
Lab. No.	Fresh meats	Desiccated meats.	Fresh meats.	Desiccated meats.	Fresh meats.	Desiccated meats.	Fresh meats	Desiccated meats	Fresh meats.	Desiccated meats
312112	11 89	12.22	2.95	2 50	1.655	1 207	0.089	0.055	. .	0.636*a*
312512	12.75	12.42	2.78	2.39	1.439	0.796	0 104	0.183	. . .	.
313812	13.45	13.65	3.11	2.66	1 534	1.050	0.090	0.101	0.507	0.342
313912	13.57	14.20	2.77	2.57	1.445	1.226	0.054	0.070	0.444	0 504
313312	14.02	14.77	3 44	3 00	1 884	1.287	0 065	0 103	. .	0 621*a*
Average	13 14	13.45	3.01	2.63	1.591	1.113	0 080	0 102	0 475	0 423

a Omitted from average.

The soluble nitrogen is distinctly lower in the desiccated meats than in the undried samples, the averages being 2.63 and 3.01%, respectively, or a percentage difference of 12.8. The fact that the percentage of soluble nitrogen is lower in each of the five samples of desiccated meat, is significant. This difference in the solubility of the nitrogen is due probably to the physical nature of the desiccated meats, since they are made up of fine particles which are hard, brittle, and horny.

The fact that the fresh samples were extracted by the centrifugal method, and the desiccated meats by the "beaker" method may be responsible for some of the differences in the percentage of soluble nitrogen in the two kinds of meat. The completeness of the extraction by the beaker method has been tested with fresh meats in this laboratory.[1]

TABLE V.—ACCUARACY OF THE WATER EXTRACTION METHOD WITH DESICCATED MEATS.*a*

	Water extracts.				
Lab. No.	I.	II.	III.	Average.	Analysts.
313512$_1$	2.520	2.571	2.578	2.556	Davis and Emmett 1912
313512$_2$	2.591	2.546	2.578	2.572	
313512$_3$	2.496	3.844*b*	2 554	2.525	
Average	2.536	2.559	2.570	2.551	
324613$_1$	2.020	2.042	1.748*b*	2.031	Davisson and Emmett 1913
324613$_2$	2.049	2.051	1.998	2.030	
Average	2.034	2.046	1.998	2.030	

a From the report of the referee (Emmett) on the separation of nitrogenous bodies in meats: U. S. Dept. Agric., Bur. Chem., *A. O. A. C.* 1912 and 1913.

b Omitted from average.

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[1] The data in Table V show that this method works well with desiccated meats.

It will be seen that the data for the heat coagulable nitrogen (Table IV) are lower in the desiccated meats. The average values are 1.113% for the dried samples, and 1.591% for the fresh samples, a difference of 30%. While the method for determining this form of nitrogen is not as accurate as that for the total, the errors due to the method, when it is carried out properly, are much less than the differences found here.

It is interesting to note that these differences between the fresh and desiccated meats, in the case of the soluble and the coagulable nitrogen are nearly the same, being 0.452 and 0.478%, respectively. In other words, it appears that one of the fundamental changes that took place during the process of the desiccation of the meats was the partial coagulation of the water-soluble protein, and as a result, the solubility of the total nitrogen was decreased.

The data for the proteose nitrogen indicate, with the exception of sample No. 312112, that there was a distinct increase of this constituent in the desiccated meats. The averages for the fresh and the desiccated samples are 0.080 and 0.102%, respectively.

This change in the proteose form is due probably, in part at least, to the action of enzymes during the preliminary drying. While it is generally admitted that the acid zinc sulfate method of determining the proteose nitrogen is far from satisfactory, the fact that four of the five desiccated samples had higher values than the corresponding fresh samples, is good evidence that the difference is due to the chemical composition of the meat rather than to the errors in the method.

Regarding the creatine data, little can be said, on account of the small number of determinations that were made on the fresh meats. The average value for the fresh meats is 0.475%, and for the desiccated meats, 0.423%.

TABLE VI.—THE PERCENTAGE OF THE FORMS OF NITROGEN IN THE FRESH AND DESICCATED MEATS.

Results Calculated to the Dry and Fat-free Basis.

	Total nitrogen.		Water-soluble nitrogen.						Creatin.	
			Total.		Coagulable.		Proteose.			
Lab. No	Fresh meats	Desiccated meats.	Fresh meats.	Desiccated meats.	Fresh meats	Desiccated meats	Fresh meats.	Desiccated meats	Fresh meats	Desiccated meats.
312112	14.27	14.91	3.54	3.05	1.99	1.47	0.107	0.134		0.776*a*
312512	14.85	14.74	3.24	2.84	1.68	0.94	0.121	0.217		.
313812	14.69	14.67	3.40	2.89	1.68	1.15	0.098	0.110	0.554	0.374
313912	14.48	15.19	2.95	2.75	1.54	1.33	0.058	0.075	0.474	0.539
313312	15.20	15.67	3.73	3.18	2.04	1.36	0.070	0.109		0.659*a*
Average	14.70	15.04	3.37	2.94	1.78	1.25	0.091	0.129	0.514	0.456

a Omitted from average.

In order to eliminate the possible influence of the variations in the percentage of fat, the data in Table III are presented on the dry and fat-free basis. These results confirm the statements that were made with reference to the relative composition of the fresh and desiccated meats, namely, that the latter samples have a slightly higher per cent. of total nitrogen and of proteose nitrogen, and a lower per cent. of total water-soluble and of heat coagulable nitrogen. The respective average values are: for total nitrogen, 14.70 and 15.04%; for proteose nitrogen, 0.091 and 0.129%; for water-soluble nitrogen, 3.37 and 2.94%, and for the heat coagulable nitrogen, 1.78 and 1.25%.

TABLE VII.—DISTRIBUTION OF THE WATER-SOLUBLE NITROGEN.

Results Expressed in Per cent. of the Total Nitrogen.

	Total soluble.		Coagulable.		Proteose.	
Lab. No.	Fresh meats.	Desiccated meats.	Fresh meats.	Desiccated meats.	Fresh meats.	Desiccated meats.
312112	24.85	20.46	13.91	9.88	0.74	0.90
312512	21.81	19.29	11.28	6.41	0.82	1.47
313812	23.16	19.69	11.40	7.83	0.67	0.75
313912	20.40	18.12	10.64	8.76	0.40	0.49
313312	24.51	20.29	13.43	8.71	0.46	0.70
Average	22.95	19.57	12.13	8.32	0.62	0.86

The distribution of the forms of water-soluble nitrogen in the two series of samples is given in Table VII, expressed in per cent. of the total nitrogen.

From the above data, the total nitrogen of the fresh meats contains a higher per cent. of water-soluble and heat coagulable nitrogen than does that of the desiccated meats, and a lower per cent. of proteose nitrogen. The respective average values are, for soluble nitrogen, 22.95 and 19.57%; for heat coagulable nitrogen, 12.13 and 8.32%; and for proteose nitrogen, 0.62 and 0.86%. In this connection, it should be noted in the case of both the total soluble and coagulable nitrogen, that the highest values in the desiccated meats are no greater than the lowest values in the fresh meats.

Summary and Conclusions.

1. In determining the dry substance in fresh and desiccated beef, the percentage values were higher with the vacuum method than with the heat method at 100–105°. The difference between the two procedures was about 1.9% of the dry substance, as determined by the vacuum method.

2. The percentage of fat (ether-soluble matter) in the dried residues from the heat and the vacuum methods was not influenced apparently by the method of drying. Since the fats, after extraction, were dried in both cases at 100°, there is a possibility that some of the fat from the vacuum-dried samples was volatilized at this stage. The average values were: for the fresh meats 3.12 and 2.98% for the vacuum and heat methods,

respectively, and for the corresponding desiccated samples, 10.28 and 10.04%.

3. Calculating the data for the forms of nitrogen to the dry basis, using the values obtained by the two methods, the results were from 1.2 to 2.0% lower in the case of the vacuum-dried samples.

4. There was no loss of nitrogen upon drying the meats at 100–105°. There was a small loss of nitrogen when the samples were heated at 130°.

5. Comparing the composition of the fresh and desiccated meats, the average percentage fat content of the samples, when calculated to the dry basis was not altered during the desiccation. The respective values were 10.31 and 10.21%. There were, however, distinct individual irregularities in some of the samples.

6. The percentage of total nitrogen in the desiccated meats was slightly higher than in the fresh samples. The respective values were, upon the dry basis, 13.14 and 13.45%, and upon the dry and fat-free basis, 14.70 and 15.04%.

7. The solubility of the nitrogen decreased upon desiccation. The average values for the desiccated meats were 3.01% on the dry basis and 3.48% on the dry and fat-free basis, while the corresponding data for the fresh meats were 2.63 and 2.94%, respectively. Expressing the per cent. of soluble nitrogen in terms of the total nitrogen, the fresh meats had 22.95% of water-soluble nitrogen, and the desiccated meats 19.57%.

8. The percentage of coagulable nitrogen was lowered during desiccation by about 30%. The average values were 1.591 and 1.113%, respectively, for the fresh and dried meats upon the dry basis, and 1.784 and 1.252% upon the dry and fat-free basis. Of the total nitrogen, 12.13% was coagulable in the fresh meats, and 8.32% in the desiccated meats.

9. There was a distinct and significant increase in the percentage of water-soluble proteose nitrogen in the desiccated meats, amounting on the average to 22% of that found in the fresh, undried meats.

Further study is contemplated along this line, and it is the intention to include other meats, differing not only in kind but in degree of fatness.

The authors gladly take this opportunity of expressing their appreciation to Professor Grindley for the helpful suggestions which he offered.

Literature.

[1] Hofmeister, *Z physiol. Chem* , **2**, 206; F. G. Benedict, *Am Chem. J* , **27**, 340; Shultz, *Archiv. f. gesammte Physiol* , **56**, 203; Gibson and Atwater, U. S. Dept. Agr., *O. E. S. Bull.* **21**; Benedict and Manning, *Am. J. Physiol.*, **13**, 325; **18**, 213; Frear and Beistle, New York Agr. Expt. Sta. (Geneva), *Bull.* **6**; Emmett and Gies, *Am. J. Physiol.*, **19**, 11; Kumagawa and Suto, *Biochem. Z.*, **8**, 212; Trowbridge, U. S. Dept. Agr., Bur. Chem., *Bull.* **122**, **132** and **137**; Shackell, *Am. J. Physiol.*, **24**, 325; Löwenstein, *J.*

Ind. Eng. Chem., 1, 252; Shimidzu, *Biochem. Z.*, 28, 237; Tamura, *Ibid.*, 41, 78; W. Koch and M. L. Koch, *J. Biol. Chem.*, 14, 281; Gore, *Ibid.*, 15, 259.

[2] Dyer, *J. Chem. Soc.*, 67, 811; Sherman, McLaughlin and Osterberg, THIS JOURNAL, 26, 367; Sherman and Falk, *Ibid.*, 26, 1469; Emmett, *Proc. Assoc. Off. Agr. Chem.*, U. S. Dept. Agr., Bur. Chem., *Bull.* 162, 145; Trescot, *J. Ind. Eng. Chem.*, 5, 914.

[3] Grindley and Emmett, THIS JOURNAL, 27, 658.

[4] Folin, *Z. physiol. Chem.*, 41, 223; also *Am. J. Physiol.*, 13, 48; Benedict and Myers, *Ibid.*, 18, 395; Emmett and Grindley, *Ibid.*, 3, 6.

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NOTE.

Uses of the Concentrated Filament Tungsten Lamp in the Laboratory.—In laboratories where much microscopic work is done, it is frequently necessary, or preferable, to depend upon artificial light; and for this purpose the Welsbach gas lamp seems to be quite generally used, while the Nernst lamp is also used to some extent, with seemingly good results. During the past few months there has been in use in this laboratory, for such work, a stereopticon type of tungsten lamp which has proven so satisfactory as to make it seem probable that a description of it may be of interest to others. The lamp is rated at 100 watts, and probably gives about 60 c. p. The filament, instead of being strung out in straight loops between the points of support, is formed into a close coil, which is looped over supports about one centimeter apart (see Fig. 2), and loops forming an open cylinder about one centimeter in diameter. Thus when looked at from the side, the entire light-giving element is concentrated in a space about one centimeter square. The lamp is provided with a round blub about 7.5 cm. in diameter.

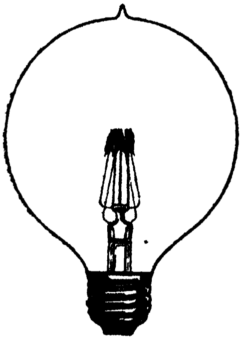
Fig. 1.

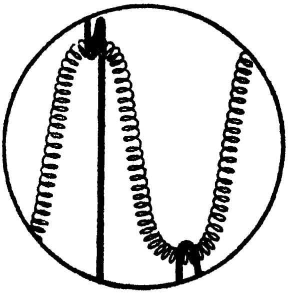
Fig. 2.

The lamp has also been used with the polarimeter for the investigation of the rotatory power of solutions which are too highly colored or which cannot be cleared by the ordinary methods and are too cloudy to transmit sufficient light from the ordinary sources for satisfactory reading. It has the advantage over the ordinary clear bulb tungsten lamp, that no bright-line images of portions of the filament are formed in the field of the instrument, and the intensity is very much greater than that obtainable with the frosted bulb lamp. No doubt other uses may be found for such a lamp in general laboratories.

The lamp is shown in the accompanying figures, and the specifications for it are as follows: Mazda, stereopticon type (concentrated filament), 100-watt, 110-volt, G-30 bulb, unskirted.

A 60-watt lamp has also been made, having a smaller bulb. So far as the writer knows, they have not been made for 220-volt circuits, though two in series could be operated at this voltage, of course.

In laboratories having the proper current, the new nitrogen-filled Mazda lamps will, no doubt, prove useful for the same purposes as the above described stereopticon lamp. This lamp is made in a 100 c. p. size, taking 10 amperes at 6 volts—about 0.6 watt per candle—in a bulb of the same size as the first lamp mentioned, the filament consisting of a single heavy loop; also for 6.6 ampere (street-series) at voltages from 6 to 50.

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NEW BOOKS.

L'Etude physico-chimique des Sels chromiques. PAR A. SÉNÉSCHAL. Nr. 5 des Publications de la Societe de Chimie-Physique, pp. 28, 1913. Paris, Librairie Scientifique, A. Hermann et Fils Price 2 francs.

The differently colored modifications of chromium chloride, nitrate, sulfate, etc., have offered an alluring problem to chemists for more than a century. Little progress was made in their study until Recoura, in 1887, resorted to methods of physico-chemical analysis.

Sénéschal in this short pamphlet reviews the work of Recoura and the physico-chemical investigations which have succeeded it in this field, displaying that lucidity of statement which is so often encountered among French writers. Of these investigations those of Werner have been of the greatest importance. His coördination theory has proven very illuminating when applied to these salts, and has furnished the only satisfactory classification of them; indeed, by its aid, we can deduce the architecture of the green hexahydrate of chromium chloride, in greater detail than is possible with almost any other inorganic compound. Werner's work and the careful measurements of Bjerrum on the rates of transformation of, and on the equilibria between, different modifications of chromium chloride in solution, constitute the principal subject matter of the pamphlet.

Since what the author gives is so well given, we regret that he did not give us more. He has ignored a number of recent investigations specifically dealing with his field; namely, those of Olie, Weinland and Koch, Graham, Pfeiffer and the most recent investigations of Werner, and others. Indeed, he has not even mentioned these investigations in his bibliography.

ARTHUR B. LAMB.

L'Addivité des Propriétés Diamagnetiques et son Utilisation dans la Recherche des Constitutions. By PAUL PASCAL. No. VI des Publications de la Société de Chimique-physique. 8°, 26 pp., 1 franc. Librairie Scientifique, A. Hermann et Fils, Paris, 1913.

In the last few years, the study of organic compounds from the point of view of magnetochemistry has developed so rapidly that its methods now promise to rank as equally important in the physico-chemical investigation of structure as those of spectrochemistry. What Brühl was in the latter field, Pascal, the author of the pamphlet before us, has made himself in the magnetochemical investigation of structure. The pamphlet is a publication of an address given last April before the Société de Chimique-physique in Paris. It presents a lucid, concise and up-to-date survey of the most important of the conclusions arrived at by this brilliant investigator. Organic chemists will be especially interested in the views presented in connection with such old friends in the arena of structure as tautomerism, residual valences, benzene, naphthalene.[1] But all chemists should be interested alike in one of the most important of the modern questions concerning the structure of the molecule, which the electron theory of valence at length promises to put on a definite experimental basis[2]—namely, the question of the influence of neighboring, but not directly linked, atoms and groups on one another: The magnetochemical method of investigation claims to be capable of measuring these effects quantitatively. For instance, it is of interest to note that in alkyl halides there is plainly manifest an attraction between the hydrogen and the halogen atoms attached to neighboring carbon atoms, an attraction so intense as to make the molecule approach decidedly toward the formation of an ethylene group--if indeed the results do not show that in a fraction of the molecules such ethylene groups have been actually formed with liberation of halogen acid.[3]

JULIUS STIEGLITZ.

CHICAGO, Dec. 15, 1913.

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[1] The author refers to Claus's and Bamberger's theories but not to that of Armstrong-Baeyer, of which Bamberger's work is an outgrowth.

[2] See, for instance, the simple and instructive application of such views to nitric acid and ammonium hydroxide by W. A. Noyes, THIS JOURNAL, 34, 663 (1913).

[3] Chemists unfamiliar with this field but interested in it, will find Wedekind's *Magnetochemie* (Borntraeger, Berlin, 1911) an excellent introduction to it, with ample references to original articles.

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TWENTY-FIRST ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1913.

BY GREGORY PAUL BAXTER

Received February 6, 1914.

The following data have been obtained in the various investigations upon atomic weights published during 1913. Since in the past similar summaries have been essentially non-critical, the results are quoted without comment in the present report.

Oxygen.—Germann[1] has redetermined the weight of the normal liter of oxygen, and has obtained a value essentially identical with the one commonly accepted.

Globe 1. 872.33 cc.	Globe 2. 455.72 cc.	Globe 3. 410.27 cc.	Globe 4. 252.004 cc.
1.42889	1.42906	1.42941	1.42941
1.42901	1.42936	1.42940	1.42906
1.42877	1.42815	1.42896	1.42837
1.42847	1.42956	1.42896	1.42915

General mean, 1.42900

Helium.—Heuse,[2] in seven experiments with a 547 cc. globe, finds the weight of the normal liter of helium to be as follows:

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[1] *Compt. rend.*, **157**, 926 (1913).

[2] *Verh. deutsch. phys. Gesell.*, **15**, 518 (1913).

	0.17845
	0.17851
	0.17868
	0.17862
	0.17825
	0.17890
	0.17853
Mean,	0.17856

By the method of limiting densities he then calculates the molecular and atomic weight of helium to be 4.002.

Chlorine and Fluorine.—Jaquerod and Tourpaian[1] have determined the densities of chlorine and silicon tetrafluoride both by displacement of the gases with a vessel of known volume, and by the use of an ordinary density globe. Measurements were made at 15–20° and about 725 mm.

	Weight of one liter of chlorine at 0° and 725 mm.
By displacement... ...	3.0630 at 15°
By displacement.... ...	3.0632 at 15°
By density globe	3.0624 at 15°
By density globe.. .. .	3.0629 at 0°
Mean,	3.0629

Corrected for the deviation from Boyle's law, the weight of the normal liter is 3.2137 grams.

	Weight of one liter of silicon tetrafluoride at 0° and 725 mm.	
By displacement...........	4.4750	3 experiments at 20°
By density globe...........	4.4757	3 experiments at 20°
By density globe...........	4.4760	3 experiments at 0°
Mean,	4.4756	

The weight of the normal liter is then calculated to be 4.6929 grams. By the methods of "corresponding densities" and "critical constants" the atomic weight of chlorine is computed to be 35.28 and 35.27, respectively, and that of fluorine 19.10 and 19.09, the atomic weight of silicon being assumed to be 28.3.

Silver, Sulfur and Chlorine.—Scheuer[2] dissolved weighed amounts of pure silver in concentrated sulfuric acid. The sulfur dioxide evolved was liquefied and weighed. The silver sulfate, after it had been fused and weighed, was changed to silver chloride in a current of hydrochloric acid gas, and the silver chloride was weighed.

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[1] *J. chim. phys.*, 11, 3, 269 (1913).

[2] *Arch. sci. phys. nat.*, [4] **36**, 381 (1913).

Wt. Ag.	Wt. SO_2.	Wt. Ag_2SO_4.	Wt. AgCl.	At wt Ag.	At. wt. S.	At. wt. Cl.
8.63592	2.56427	12 48100	11 47436	107 881	32.066	35.458
5.99316	1.77946	8 66142	7 96296	107 888	32.067	35.460
10.21124	3.03204	14.75768	13 56757	107 884	32.069	35.460
8.96085	2.66050	12.95023	11 90590	107.891	32.066	35.459
9.70232	2 88105	14 02239	12.89159	107 877	32.067	35 460
			Mean,	107 884	32 067	35.460

Silver.—Richards and Cox[1] have shown it to be improbable that lithium perchlorate, as prepared by Richards and Willard in their work upon the atomic weights of silver and lithium, contains any residual water. The value for the atomic weight of silver obtained by the latter, 107.871, therefore needs no correction.

Calcium.—The atomic weight of calcium has been determined by Oechsner de Coninck[2] by the conversion of weighed amounts of calcium carbonate into calcium sulfate, with the following results:

Weight $CaCO_3$	Weight $CaSO_4$.	At. wt. Ca.
0.3300	0 4486	40.16
0 2640	0 3590	40 04
0 3630	0 4935	40 13
0 2541	0 3454	40 19
0 1524	0 2072	40.11
	Mean,	40 13

Barium.—Oechsner de Coninck[3] has also determined the atomic weight of barium through the carbonate by weighing the carbon dioxide evolved with nitric acid. The value 137.36 was obtained.

Radium.—Hönigschmid[4] has published additional data upon the analysis of radium bromide, and for sake of completeness all his results with the above salt are quoted below. In some analyses silver bromide was precipitated and weighed, in others the radium bromide was compared with silver. Ag = 107.880. Br = 79.916.

Weight $RaBr_2$.	Weight AgBr.	At. wt. Ra.
1.17016	1.13940	225.90
0.99658	0 97022	225 97
0 90111	0 87733	225.94
0 75504	0.73502	225.98
0.72731	0 70810	225.95
0 60329	0 58734	225 96
1 08458	1 05588	225.97

Mean, omitting the first, 225 96

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[1] *Com. Eighth Internat. Cong. Appl. Chem.*, **25**, 157 (1913).

[2] *Bull. belg. acad.*, **1913**, 222.

[3] *Rev. gén. chim.*, **16**, 245 (1913).

[4] *Sitzungsb. kais. Akad. Wien.*, **121**, Abt IIa 1973 (1912); *Monatsh Chem*, **34**, 283 (1913).

Weight $RaBr_2$.	Weight Ag.	At. wt. Ra.
0.68496	0.38306	225.97
0.60329	0 33739	225.97
		Mean, 225.97

For sake of comparison with Gray and Ramsay's method, Hönigschmid in two experiments converted radium bromide into radium chloride by heating in a current of hydrochloric acid gas. Cl = 35.457.

Weight $RaBr_2$.	Weight $RaCl_2$.	At. wt. Ra.
0.12885	0.09915	225.93
0.93192	0 71712	225.94

Hönigschmid also points out that Gray and Ramsay added the vacuum corrections to the weights of their salts instead of subtracting them, as was necessary since their weights were of quartz. Gray and Ramsay's results, when corrected for this error, are widely discrepant and deviate less from Hönigschmid's than the uncorrected.

Weight $RaBr_2$. Mg.	Weight $RaCl_2$. Mg.	At. wt. Ra.
2.85238	2 19536	226.20
2.76046	2.12422	225.95
2 61007	2 00922	226.42
2 43259	1.87213	226.11
2 35986	1 81687	226.61
		Mean, 226.26

The mean of Hönigschmid's results from analyses of the chloride and bromide is 225.96. To this value, however, must be added 0.01 as a correction for the temperature of the radium preparations, so that the final outcome of Hönigschmid's researches is the value 225.97 for the atomic weight of radium.

Cadmium.—Laird and Hulett[1] simultaneously electrolyzed cadmium and silver solutions. The cadmium was deposited in mercury in platinum vessels, and the silver on gold or platinum. The silver deposit was corrected for inclusions. Ag = 107.88. Vacuum weights are given.

Weight Cd.	Weight Ag.	At. wt. Cd.
2.2721	4.3638	112.340
2.2733		112.400
2.3549	4.5225	112.352
2.3534		112.276
2.6637	5.1186	112.280
2.6656		112.358
1.9937	3.8312	112.280
1.9938		112.288

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[1] *Trans. Amer. Elect. Soc.*, **22**, 385 (1912).

Weight Cd.	Weight Ag.	At. wt. Cd.
2.2979 2.2972	4.4148	112.302 112.268
2.4265 2.4261	4.6605	112.336 112.318
2.1496 2.1501	4.1297	112.308 112.334
2.6679 2.6675	5.1256	112.304 112.288
		Mean, 112.313

This low result for the atomic weight of cadmium is in accord with the value 112.30 previously obtained by Perdue and Hulett and has been confirmed by Quinn and Hulett,[1] who determined electrolytically the cadmium content of fused cadmium chloride and bromide. After the salts were weighed they were converted into sulfate, and the cadmium was deposited in mercury in a platinum vessel. Weights are corrected to vacuum. Cl = 35.458. Br = 79.92.

Weight $CdCl_2$.	Weight Cd.	At. wt. Cd.
4.10119	2.51427	112.36
4.47151	2.74084	112.31
5.66452	3.47180	112.28
5.99291	3.67211	112.20
6.52910	4.00219	112.32
4.87415	2.98785	112.33
4.88423	2.99384	112.31
		Mean, 112.32

Weight $CdBr_2$.	Weight Cd.	At. wt. Cd.
4.95538	2.04468	112.28
4.15801	1.71573	112.29
5.31272	2.19183	112.26
4.31525	1.78013	112.24
4.55544	1.87940	112.26
5.69646	2.34983	112.23
4.47748	1.84754	112.29
5.36276	2.21228	112.24
		Mean, 112.26

Mercury.—Taylor and Hulett[2] synthesized mercuric oxide by heating mercury in oxygen. Weighed amounts were then decomposed at a high temperature with metallic iron, and the mercury was weighed.

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[1] *J. Physic. Chem.*, **17**, 780 (1913).

[2] *Ibid.*, **17**, 755 (1913).

Weight HgO.	Weight Hg.	At. wt. Hg.
2.98464	2.76390	200.33
3.61841	3.35066	200.25
3.82184	3.53923	200.39
3.40356	3.15185	200.36
3.80726	3.52567	200.39
4.56858	4.23065	200.30
5.42945	5.02819	200.48
2.38313	2.20681	200.28
3.76766	3.48933	200.57
		Mean, 200.37

Scandium.—Lukens[1] extracted scandium material from Colorado wolframite. The purified salt showed no evidence of radioactivity, and its spark spectrum contained only scandium lines. Weighed amounts of anhydrous sulfate were calcined to oxide.

Weight $Sc_2(SO_4)_3$.	Weight Sc_2O_3.	At. wt. Sc.
0.30636	0.11134	44.59
1.14140	0.41553	44.77
		Mean, 44.68

Yttrium.—Three researches upon the atomic weight of yttrium have appeared during the past year. Egan and Balke[2] purified yttrium material by crystallization of the bromate and by fractional precipitation of the chromate, but spectroscopic examination showed a small proportion of erbium still to be present. After comparison of different methods, that of converting weighed amounts of yttrium oxide into anhydrous chloride was adopted. Cl = 35.46.

Weight Y_2O_3.	Weight YCl_3.	At. wt. Y.
0.72180	1.24092	90.54
0.80392	1.38437	90.10
0.70050	1.20610	90.14
0.73030	1.25755	90.11
		Mean, 90.22

R. J. Meyer and Wuorinen[3] freed yttrium material from other rare earths by fractional precipitation of the impurities with potassium iodate. Five syntheses of yttrium sulfate from the oxide yielded the following results, no correction being made for the retention of acid by the anhydrous sulfate. S = 32.0.

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[1] THIS JOURNAL, **35**, 1470 (1913).

[2] *Ibid.*, **35**, 365 (1913).

[3] *Z. anorg. Chem.*, **80**, 7 (1913).

Weight Y_2O_3.	Weight $Y_2(SO_4)_3$.	At. wt. Y.
0.5096	1.0534	88.46
0.5126	1 0592	88 54
0 5491	1 1347	88 52
0.5071	1.0479	88 52
0.7234	1 4950	88 50
		Mean, 88.51

In two additional analyses the sulfuric acid retained by the sulfate was determined, and the necessary correction applied.

Weight Y_2O_3.	Weight $Y_2(SO_4)_3$.	At. wt. Y.
0.5544	1.1452	88 60
0.9003	1 8595	88 64
		Mean, 88 62

The purified material contained spectroscopic traces of several rare earths.

In a subsequent paper, R. J. Meyer and Weinheber[1] correct the results of Meyer and Wuorinen by recalculating them on the basis S = 32.07, and give the results of three experiments with new material purified as by the latter.

Weight Y_2O_3.	Weight $Y_2(SO_4)_3$.	At. wt. Y.
0.5544	1.1452	88.71
0 9003	1.8595	88.73
0 4954	1 0231	88.76
0.4972	1 0266	88 80
0 4980	1 0286	88 73
		Mean, 88 75

In another series of experiments Meyer and Weinheber calcined weighed amounts of anhydrous sulfate to oxide.

Weight $Y_2(SO_4)_3$.	Weight Y_2O_3.	At. wt. Y.
1.0248	0.4962	88 74
0.8585	0.4157	88 75
1 4060	0 6808	88 75
0.8944	0 4330	88 71
0.9795	0.4743	88 76
0.5686	0.2753	88.73
		Mean, 88.74

The above weights are not corrected to the vacuum standard. When this correction is made, the atomic weight of yttrium becomes 88.70.

Ytterbium.—Auer von Welsbach[2] has continued the fractionation of aldebaranium and cassiopeium material and has determined the atomic weights of both by precipitating the oxalate from weighed amounts of the hydrated sulfate, and igniting the oxalate to oxide.

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[1] *Ber.*, **46**, 2672 (1913).

[2] *Monatsh. Chem.*, **34**, 1713 (1913).

Weight $Cp_2(SO_4)_3.8H_2O$.	Weight Cp_2O_3.	At. wt. Cp.
2.0428	1.0394	175.06
2.0197	1.0274	174.96
2.4044	1.2232	175.00
		Mean, 175 00

Weight $Ad_2(SO_4)_3.8H_2O$.	Weight Ad_2O_3.	At. wt. Ad.
2.0530	1.0392	172.98
2.0891	1.0575	172.99
2.1155	1.0710	173.04
		Mean, 173.00

Selenium.—Bruylants and Bytebier[1] prepared selenium hydride by the action of water upon aluminum selenide and after the purification of the gas determined the weight of the liter at 0° and 760 mm., uncorrected for the force of gravity at Louvain, to be as follows:

	Globe 1. 410 cc.	Globe 2. 503 cc.	Globe 3. 603 cc.	Globe 4. 1006 cc.
	3.67108	3.67101	3.67215	3.67120
	3.67128	3.67101	3.67074	3.67243
	3.67141	3.67132	3.67163	3.67106
	3.67096	3.67110	3.67142	3 67216
	....	....	3.67246	3 67240
Mean,	3 67118	3 67111	3.67168	3.67185
			General mean,	3 6715

For purposes of comparison, Bruylants and Bytebier also determined the weight of a liter of oxygen under the same conditions.

Globe 1.	Globe 2.	Globe 3.	Globe 4.
1.42941	1.42977	1.42933	1.42942
1.42969	1.42932	1.42926	1 42980
.....	1.42921	.....	1 42966
		General mean,	1.4295

By the method of limiting densities the molecular weight of selenium hydride is computed to be 81.196, and the atomic weight of selenium, therefore, to be 79.18. (H = 1.008.)

Jannek and J. Meyer[2] have determined directly the ratio of selenium to oxygen by oxidizing weighed amounts of the element to the dioxide. The selenium was heated in a quartz vessel in a current of dry oxygen and nitrogen peroxide. To show that no material was lost by vaporization during the process, in three experiments the dioxide was dissolved, the selenium precipitated by dilute hydrazine, collected upon a Neubauer crucible and weighed. The maximum difference between the selenium used and that recovered was 0.00003 gram. The following weights are reduced to the vacuum standard:

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[1] *Bull. Belg. Acad.*, 1912, 856.

[2] *Z. Electroch.*, 19, 833 (1913); *Z. anorg. Chem.*, 83, 51 (1913).

Weight Se.	Weight SeO_2.	At. wt. Se.
2.32307	3.26249	79.132
2.00162	2.81083	79.151
2.14178	3.00789	79.132
3.29634	4.62932	79.135
2.10447	2.95522	79.152
4.82540	6.77635	79.148
5.91515	8.30670	79.146
2.43479	3.41935	79.135
2.95206	4.14583	79.133
3.27487	4.59907	79.140
	Mean,	79.140

Tellurium.—Dudley and Bowers[1] reject as unsatisfactory the basic nitrate method of determining the atomic weight of tellurium and find the synthesis of the tetrabromide from the metal far more satisfactory. Five preliminary experiments with the same specimen of material give the following results (vacuum weights). Br = 79.92.

Weight Te.	Weight $TeBr_4$.	At. wt. Te.
0.479816	1.682387	127.550
0.296341	1.037049	127.897
0.433241	1.516746	127.819
0.457782	1.605684	127.487
0.321522	1.126939	127.612
	Mean,	127.673

Six final determinations were made with three different fractions.

Weight Te.	Weight $TeBr_4$.	At. wt. Te.
0.300558	1.054251	127.481
0.199807	0.700947	127.456
0.22032	0.773048	127.425
0.158161	0.554717	127.500
0.436907	1.532360	127.500
0.29811	1.045485	127.512
	Mean,	127.479

Copper.—The atomic weight of copper has been found by Oechsner de Coninck and Ducelliez[2] by dissolving weighed amounts of metal in nitric acid and igniting the residue after evaporation. Four results, which vary from 63.523 to 63.605, give an average value of 63.549.

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[1] THIS JOURNAL, **35**, 875 (1913).

[2] *Rev. gén. chim.*, **16**, 122 (1913).

Iridium.—The atomic weight of iridium has been determined by Holzmann[1] by reduction of ammonium chloroiridiate in a current of hydrogen. The following weights are reduced to the vacuum standard. H = 1.008. N = 14.01. Cl = 35.46.

Weight $(NH_4)_2IrCl_6$.	Weight Ir.	At. wt. Ir.
1.09292	0.47809	193.50
1.15060	0.50299	193.27
0.80293	0.35126	193.52
0.78021	0.34119	193.39
		Mean, 193.42

Guye[2] compares critically the various methods employed in atomic weight investigations, and pleads for a more systematic attack on the problem from many quarters. Guareschi[3] calls attention to the universal presence of bromine in compounds of chlorine and iodine. Several articles have appeared dealing with the relations between the different atomic weights.[4]

THE ACCELERATION OF ELECTRICAL CONDUCTORS.

BY RICHARD C. TOLMAN, EARL W. OSGERBY AND T. DALE STEWART.

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Part II. *Metallic Conductors:* 1. Introduction. 2. The Apparatus. 3. The Experimental Work. 4. Results. 5. Conclusion.

PART I. ACCELERATED ELECTROLYTES.

(Experimental Work Performed in the Chemical Laboratory of the University of Cincinnati by R. C. Tolman and E. W. Osgerby.)

1. Introduction.

The force of gravity has been found to produce a difference in electrical potential between the two ends of a vertical tube of salt solution.[1] This difference in potential evidently arises from the unequal weights of the positive and negative carriers of electricity in the solution. Thus the lower end of a tube of potassium iodide solution becomes negatively charged, since the negative iodide ions are heavier than the positive potassium ions.

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[1] *Sitzungsb., Phys.-med. Soz. Erlangen,* **44**, 84 (1912).

[2] *J. chim. phys.,* **11**, 275 (1913).

[3] *Atti accad. sci. Torino,* **48**, 128 (1913).

[4] Bilecki, *Z. physik. Chem.,* **82**, 249; Borodovskii, *Chem. Ztg.,* **36**, 198; Büry, *Z. physik. Chem.,* **80**, 381; Dambier, *J. chim. phys.,* **11**, 260; Guye, *Ibid.,* 267; Feilmann, *Chem. News,* **107**, 15; Katayama, *Sci. Rep'ts Tohoku Imp. Univ. Sendai,* **1**, 171; Loring, *Chem. News,* **107**, 193; **108**, 95; Moir, *J. Chem. Met. Soc. S. Africa,* **13**, 544; Wilde, *Chem. News,* **108**, 52.

In a similar way we should expect a tube of solution, when subjected to *acceleration*, to show a difference in potential between the two ends. For example, the rear end of a tube of potassium iodide solution should show a negative charge as long as the tube is being accelerated.

The purpose of Part I of this article is to describe some measurements made on accelerated solutions of potassium, sodium and lithium iodides, and to show that the results obtained are in satisfactory agreement with those predicted on a theoretical basis. In Part II of the article we shall apply similar theoretical considerations to the case of accelerated metals and describe the progress that has been made towards an experimental solution of the problem.

2. The Theory of an Accelerated Solution.

If a tube of liquid which has the density d grams per cubic centimeter be given an acceleration a, it is evident that the force acting on any cubic centimeter of the liquid must be $f = da$ in order to produce the acceleration. Since this force is transmitted to the cubic centimeter in question by the surrounding liquid, it is evident that this space might be filled with a cubic centimeter of any other material without changing the magnitude of the force. Hence for a solution, the force acting on one equivalent of solute during acceleration would be $A\bar{v}da$, where A is the equivalent weight of the solute, $\bar{v}$ its partial specific volume, d the density of the solution and a the acceleration of the solution as a whole. We shall call this force, whose magnitude depends merely on the displaced volume, the *buoyant force* acting on the solute.

If the solute in question carries an electrical charge there may be an additional *electrical force* acting on the solute. If F is the charge in coulombs carried by one equivalent, the electrical force acting on each equivalent of solute will be $10^7F\ dE/dl$ dynes where dE/dl is the potential gradient in which the solute finds itself.

In general, besides the above forces, there will be a *frictional force* acting on each equivalent of dissolved substance. The fact that Ohm's law holds for electrolytes shows that for ionic solutes this frictional force is proportional to the velocity of the ionic substance through the rest of the solution. If U is the velocity which one equivalent of ionic constituent attains under unit force, then, when the relative velocity of solute and solution is u, the frictional force acting will be u/U.

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[1] See Tolman, THIS JOURNAL, 33, 121 (1911), for a review of the work in this field.

Consider now, a tube filled with a solution of potassium iodide. The tube is provided at the two ends with platinum electrodes and a small amount of iodine is also dissolved in the solution so that the electric current will enter and leave the solution at anode and cathode according to the reactions:

$$\oplus + \overset{-}{\mathrm{I}} = {}^1/_2\mathrm{I}_2 \qquad\qquad {}^1/_2\mathrm{I}_2 = \overset{-}{\mathrm{I}} + \oplus$$

An external connection is made between the two electrodes through a galvanometer.

Let l be the distance between the electrodes,

q the uniform cross section of the tube,

a the acceleration of the tube (in the direction of the line connecting the electrodes),

d the density of the solution,

C its concentration in equivalents per cc.,

$\bar{v}_{\mathrm{K}}$, $\bar{v}_{\mathrm{I}}$, $\bar{v}_{\mathrm{KI}}$ and $\bar{v}_{\mathrm{I}_2}$ the partial specific volumes of the respective solutes,

K, I, KI and I_2 their atomic or molecular weights,

$\mathrm{U_K}$ and $\mathrm{U_I}$ the velocities which the positive and negative ion constituents attain in a stationary solution when acted on by unit force per equivalent weight of ion,

$n_c = \dfrac{\mathrm{U_K}}{\mathrm{U_K} + \mathrm{U_I}}$ the transference number of the cation,

u_{K} and u_{I} the velocities with which the positive and negative ion constituents are lagging behind the solution as a whole,

R the resistance of the solution,

R_e the resistance of the external circuit,

I_c the current flowing,

f_{K} the force acting on one equivalent of potassium,

f_{I} the force acting on one equivalent of iodine.

From the preceding discussion, it is evident that the force f_{K} acting on each equivalent of potassium must be equal to the sum of the buoyant, electrical and frictional forces, leading to the equation:

$$f_{\mathrm{K}} = \mathrm{K}\bar{v}_{\mathrm{K}}da - 10^7\mathrm{F}\frac{\mathrm{E}_1}{l} + \frac{u_{\mathrm{K}}}{\mathrm{U_K}}$$

where E_1 is the difference in potential between portions of the solution in the neighborhood of the two electrodes. Multiplying through by $n_c = \dfrac{\mathrm{U_K}}{\mathrm{U_K} + \mathrm{U_I}}$ we obtain:

$$n_c f_{\mathrm{K}} = n_c\mathrm{K}\bar{v}_{\mathrm{K}}da - 10^7\mathrm{F}n_c\frac{\mathrm{E}_1}{l} + \frac{u_{\mathrm{K}}}{\mathrm{U_K} + \mathrm{U_I}} \qquad (1)$$

Similarly for the iodide ion constituent we have:

$$f_{\mathrm{I}} = \mathrm{I}\bar{v}_{\mathrm{I}}da + 10^7\mathrm{F}\frac{\mathrm{E}_1}{l} + \frac{u_{\mathrm{I}}}{\mathrm{U}_{\mathrm{I}}}$$

It should be noted that the electrical force is evidently in the same direction as the other forces for the negative ion and in the opposite direction for the positive ion.

Multiplying through by $(1 - n_c) = \frac{\mathrm{U}_{\mathrm{I}}}{\mathrm{U}_{\mathrm{K}} + \mathrm{U}_{\mathrm{I}}}$ we obtain:

$$(1 - n_c)f_{\mathrm{I}} = (1 - n_c)\mathrm{I}\bar{v}_{\mathrm{I}}da + (1 - n_c)10^7\mathrm{F}\frac{\mathrm{E}_1}{l} + \frac{u_{\mathrm{I}}}{\mathrm{U}_{\mathrm{K}} + \mathrm{U}_{\mathrm{I}}} \qquad (2)$$

Subtracting (1) from (2), solving for E_1, and simplifying, by putting the sum of the forces acting on one equivalent of the positive and negative ion constituents $(f_{\mathrm{K}} + f_{\mathrm{I}})$ equal to f_{KI}, the force acting on one equivalent of potassium iodide, and further noting that $\mathrm{K}\bar{v}_{\mathrm{K}} + \mathrm{I}\bar{v}_{\mathrm{I}} = \mathrm{KI}\bar{v}_{\mathrm{KI}}$, we obtain for E_1 the value

$$\mathrm{E}_1 = \frac{l}{10^7\mathrm{F}}\left\{f_{\mathrm{I}} - n_c f_{\mathrm{KI}} - \mathrm{I}\bar{v}_{\mathrm{I}}da + n_c\mathrm{KI}v_{\mathrm{KI}}da\right\} - \frac{l}{10^7\mathrm{F}}\,\frac{(u_{\mathrm{I}} - u_{\mathrm{K}})}{(\mathrm{U}_{\mathrm{K}} + \mathrm{U}_{\mathrm{I}})}. \qquad (3)$$

We shall be interested, however, in the total electromotive force which drives the current through the external resistance of the galvanometer, and to this value of E_1, which is merely the potential difference between the portions of solution at the two ends of the tubes, we shall add the electromotive force E_2, arising from the potential differences between the electrodes and the solution in their neighborhood. This electromotive force E_2 arises from the difference in hydrostatic pressure under which the electrode reactions take place at the two electrodes, and can easily be calculated on thermodynamic grounds.

The difference in hydrostatic pressure at the two ends of the tube is *lda*. The electrode reaction is $(\widehat{+}) + \bar{\mathrm{I}} = {}^1/_2\mathrm{I}_2$ and is accompanied by the volume change $\mathrm{I}(\bar{v}_{\mathrm{I}_2} - \bar{v}_{\mathrm{I}})$

The electromotive force E_2 is given by the equation

$$10^7\mathrm{E}_2\mathrm{F} = -\mathrm{I}(\bar{v}_{\mathrm{I}_2} - \bar{v}_{\mathrm{I}})lda, \qquad (4)$$

which is obtained by equating the external electrical work obtainable when one Faraday of electricity flows through the solution with the corresponding internal work.

Adding E_1 and E_2 we obtain an expression for E, the total potential difference between the terminals of the external circuit:

$$\mathrm{E} = \mathrm{E}_1 + \mathrm{E}_2 = \frac{l}{10^7\mathrm{F}}\left\{f_{\mathrm{I}} - \mathrm{I}\bar{v}_{\mathrm{I}_2}da - n_c f_{\mathrm{KI}} + n_c\mathrm{KI}\bar{v}_{\mathrm{KI}}da\right\} - \frac{l(u_{\mathrm{I}} - u_{\mathrm{K}})}{10^7\mathrm{F}\,(\mathrm{U}_{\mathrm{K}} + \mathrm{U}_{\mathrm{I}})} \qquad (5)$$

To simplify we may note that $u_{\mathrm{I}}\mathrm{C}q$ is the number of equivalents of iodide crossing any boundary in the solution per second, so that the current flowing through the solution, $I_c = (u_I - u_K)CqF$. Furthermore, $10^7F(U_I + U_K)CF$ is evidently the specific conductance of the solution, since it is the current which would flow through a unit cube of the solution with unit potential drop. We may write:

$$\frac{l(u_I - u_K)}{10^7F\,(U_I + U_K)} = \frac{l(u_I - u_K)CqF}{10^7F\,(U_I + U_K)CqF} = I_cR \qquad (6)$$

We may also write for E the difference in potential between the two terminals of the external circuit,

$$E = I_cR_e \qquad (7)$$

where R_e is the external resistance.

Substituting equations (6) and (7) in (5) and solving for I_e we obtain

$$I_c = \frac{l}{10^7F(R+R_e)}\left\{f_I - Iv_I da - n_c f_{KI} + n_c KIv_{KI}da\right\}$$

where I_c is the instantaneous value of the current flowing in the circuit. If we multiply through by dt and integrate over a time long enough so that the solution comes to its final steady condition, we may substitute for $\int I_c dt$ the total electricity Q in coulombs which passes, for $\int f_I dt$ the total momentum Iu attained by the iodide ion constituent, u being the final velocity of the tube. Similarly for $\int f_{KI}dt$ we may substitute KIu, and for $\int a dt$ we may substitute u the final velocity. This leads to the final equation which we shall test:[1]

$$Q = \frac{lu}{10^7F(R+R_e)}\left\{(1 - v_I d) - n_c KI(1 - v_{KI}d)\right\} \qquad (8)$$

3. The Apparatus.

The apparatus used by the authors for accelerating electrolytes consisted essentially of a glass tube provided with electrodes and bent to fit the rim of an ordinary bicycle wheel. The tube was filled with electrolyte, the wheel given a sudden acceleration, and the current noted which flowed through a galvanometer placed in the external circuit which connected the two electrodes.

(*a*) *The Glass Tube.*—The apparatus is shown somewhat diagrammatically in Fig. 1. The glass tube *A* was about two feet in diameter and was provided with platinum electrodes *B* sealed in at different points.

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[1] With regard to the theory which we have here developed for accelerated electrolytic solutions, it should be noted that the same final results could be obtained with somewhat less elaborate calculation if we should first start out by assuming that the electromotive force developed by the acceleration is equal to that which would be developed if the same tube were set up vertically in a gravitational field, the strength of the gravitational field being such that each particle is acted on by the force ma where m is its mass and a the acceleration of the tube. Such a method of considering accelerated electrolytes was used by Colley, *Wied. Ann.*, 17, 55 (1882).

By closing the stopcock C the electrolyte could be given the same acceleration as the tube, while by leaving the stopcock open the liquid could be stirred by the acceleration of the tube. Filling was done through the stopcock D. The tube was fastened to the rim of the wheel by electric tape. The circumference at the centre line of the tube was 207.3 cm., the distance between the electrodes that were furthest apart 190.8 cm., and between the nearest electrodes 66.4 cm.

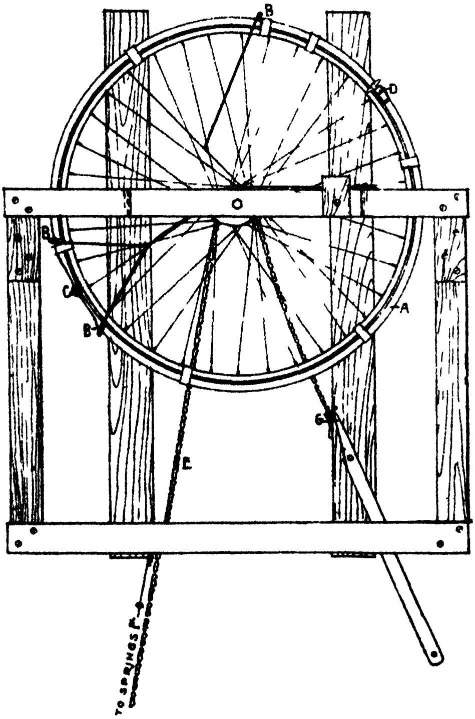

Fig 1

(*b*) *The Wheel.*—The wheel was an ordinary, metal rimmed, rear bicycle wheel with sprocket and coaster brake. The sprocket chain E passed from a pair of heavy springs F around the sprocket to the trigger G. The springs could be elongated by "winding up" the wheel and the trigger inserted in the desired link. By releasing the trigger the wheel could be accelerated and later brought to rest, with the coaster brake, by pulling back the free end of the chain. To keep the chain in position a small pull was always kept on its free end by weights attached to a cord which passed over a pulley.

(*c*) *The Springs.*—Two springs were used, connected in parallel. They were close springs, $17^1/_2''$ long, made of $^1/_4''$ wire. With the help of a turnbuckle their extension could be adjusted to any desired amount, which was always measured.

(*d*) *The Electrical Connections.*—Connection with the galvanometer was made by small size flexible electric cords, which led from the electrodes to the hub of the wheel, and then passed over suitably placed pulleys to the connections of the galvanometer. Enough slack was allowed so that the cords could wind up on the hub when the wheel was revolving. This slack was kept taut by a suitable weight. It may be specially noted that this method of connection introduces no sliding contacts. Later references will be made to this important point.

(*e*) *The Galvanometer.*—The galvanometer was a Leeds and Northrup, Type H, with a resistance of about 1300 ohms. It was mounted on a very satisfactory stone pier and showed *absolutely no motion* unless current was passed. It proved much more satisfactory than a suspended magnet galvanometer of presumably greater sensitiveness but much less stability. It was connected directly in series with the electrodes, and was observed with a telescope, at about 1.15 meters distance.

(*f*) *The Speed Measuring Device.*—The speed was measured on a revolving drum provided with smoked paper upon which simultaneous marks were made by a pointer driven by a tuning fork of known period and by a pointer actuated through an electric contact which was made once in each revolution of the bicycle wheel.

4. The Experimental Procedure.

In the experiments to be described, measurements were made on solutions of potassium, sodium and lithium iodides. The solutions contained per kilogram of water, one mol of the salt and one hundredth of a mol of iodine. The tube was rinsed with the solution before filling. In carrying out the measurements one experimenter observed the galvanometer through the telescope and the other operated the wheel. With each solution a large number of successive accelerations were made.

(*a*) *The Galvanometer Deflections.*—Owing to unavoidable differences in the conditions at the two electrodes, there was generally some current flowing through the galvanometer even when the tube was stationary, and a reading was always made immediately before releasing the trigger. In the record of experiment results this is called the "*Original Deflection*" of the galvanometer.

Upon releasing the trigger there was a sudden change in the galvanometer deflection. In the record of experimental results this is called the "*Galvanometer Throw.*" This "throw" presumably corresponded to the acceleration of the electrolyte, and for a given electrolyte, acceleration, and distance between electrodes it was approximately constant.

The "galvanometer throw" was in general followed by a slower change in deflection which presumably corresponded to an accidental variation in the conditions around the two electrodes produced by the jar of acceleration. In the record of experimental results this is called the "*Secondary Deflection*" of the galvanometer. As might be expected, the "secondary deflection" tended to be large when the "original deflection" was large. In a series of successive runs, the starting and stopping of the tube usually seemed to equalize the variations at the two electrodes and in a gratifying way decrease the size both of the "original" and the "secondary deflections."

In general, there was not much difficulty in distinguishing between the sudden "galvanometer throw," which was always in one direction, and the slower "secondary deflection" which might be in either direction. If the "secondary deflection" happened to be in the same direction as the "galvanometer throw" they sometimes merged indistinguishably one into the other. If the "secondary deflection" was in the opposite direction to the "galvanometer throw," it made the end point of the "galvanometer throw" advantageously sharp and distinct. In many cases the "secondary deflection" was absent or indistinguishable from the natural return of the galvanometer to its original position. In all other cases the nature of the secondary throw is stated in the record. Almost never did anything happen to make the "throw" of the galvanometer, even for a single acceleration, in the opposite direction to that predicted on the expectation that the heavy iodide ion would make the rear electrode negative. As complete experimental data are presented in the next section of the article, the reader can judge for himself as to the reality and magnitude of the effect reported.

Under favorable circumstances an effect could, of course, also be observed on suddenly stopping the wheel. This was not, however, suitable for purposes of measurement since, owing to the variable "secondary deflection", the galvanometer was obviously not very stationary when the wheel had to be stopped.

(*b*) *The Standardization of the Galvanometer.*—Since the period of the galvanometer was long compared with the time necessary for accelerating the tube, it was assumed that the "galvanometer throw" was proportional to the quantity of electricity whose measurement was desired. The galvanometer was calibrated by discharging a standard solenoid through it, placing in series varying amounts of resistance to correspond to the varying resistances of the different solutions. Results of the standardization are given in Table I; the value for infinite resistance was obtained by discharging a condenser through the galvanometer. Measurements

TABLE I.

Standardization of the Galvanometer.

May 27 and 28, 1913.

Resistance in series with galvanometer. Ohms	Quantity of electricity discharged through galvanometer. Coulombs × 10^{-8}.	Galvanometer throw. Millimeters.	Sensitiveness. Coulombs × 10^{-8} per millimeter
15	25.65	29.0	0.885
315	20.95	27.6	0.759
515	18.66	26.6	0.701
715	16.82	25.5	0.660
1015	14.66	24.2	0.605
1215	13.50	23.3	0.579
1415	12.50	22.6	0.553
1515	12.07	22.1	0.546
1715	11.27	21.5	0.524
1915	10.57	20.9	0.506
2015	10.26	20.4	0.503
∞	10.19	39.7	0.257

were also made which showed that the galvanometer throw, with a given resistance in the circuit, was at least approximately proportional to the quantity of electricity discharged.

(*c*) *Determination of the Speed.*—Corresponding to each series of accelerations, and in many cases both before and after the series, a number of determinations were made of the speed attained by the wheel with the same extension of the springs as that employed for the electrical measurements. It was found in general that the speed attained was always

TABLE II.

Standardization of Tuning Fork.

(About May 4, 1912).....	$135^1/_2$	$134^1/_2$	131	133	130	vibrations per second
(May 29, 1912)..........	$133^1/_4$	134	132	$128^1/_4$	$134^1/_4$	vibrations per second

Average, 1 second = 132.6 vibrations.

1 vibration = 7.55×10^{-3} seconds.

TABLE III.

Standardization of Spring.

Date.	Extension of spring.	No. tuning fork vibr., 1st revol.	No. tuning fork vibr., 2nd revol.
May 23, 1912.................	$5^3/_8$	21	$21^1/_4$
	$5^3/_8$	$20^1/_2$	..
	$5^3/_8$	$20^3/_4$	21
	$5^3/_8$	21	21
May 27, 1912.................	$5^3/_8$	$20^1/_2$	$20^3/_4$
	$5^3/_8$	$20^1/_2$	$20^1/_2$
	$5^3/_8$	$20^1/_2$	$20^1/_2$
	$5^3/_8$	$20^1/_2$	$20^1/_2$
May 28, 1912.................	$5^3/_8$	21	21
	$5^3/_8$	$20^1/_2$	21
	$5^3/_8$	$20^3/_4$	21
May 30, 1912.................	$5^3/_8$	$20^1/_2$	21
	$5^3/_8$	$20^3/_4$	21
	$5^3/_8$	$20^1/_2$	..
May 27.....................	$2^3/_4$	$35^1/_2$	..
	3	$33^1/_4$	..
	$2^1/_4$	$41^1/_4$	$44^3/_4$
	$2^1/_4$	42	46
	$2^1/_4$	$42^1/_4$	$46^1/_2$
	$2^1/_4$	$41^3/_4$	45
May 28.....................	$2^1/_4$	$44^1/_2$	$50^1/_2$
	$2^1/_4$	$43^3/_4$	47
	$2^1/_4$	45	..
May 31.....................	6	19	19
	7	$16^1/_4$	$16^1/_2$
	7	$16^1/_4$	$16^1/_2$
	7	$16^1/_2$	$16^1/_2$

Extension of spring, $2^1/_4''$, 3.09 revolutions per second.

Extension of spring, $5^3/_8''$, 6.42 revolutions per second.

Extension of spring, $7''$, 8.11 revolutions per second.

closely the same when the spring was given the same extension. In all the runs the "wound up" wheel was so set as to make nearly a complete revolution before making the first electrical contact, with its corresponding mark on the cheimograph. By counting the number of tuning fork vibrations between marks, it was found in general that the first of the successive revolutions was the fastest, although the speed usually fell off but slowly. For our calculations we shall consider the maximum speed as that obtained from the first recorded revolution.

The tuning fork was standardized against a seconds pendulum belonging to the Physics Department of the University of Cincinnati and the data therefore is presented in Table II. Table III presents the data for the speed attained with different extensions of the spring.

5. The Experimental Results.

The main part of the experimental work consisted in a series of measurements with molal solutions of potassium, sodium and lithium iodides, all made with the same deflection of the springs $5^3/_8''$, and with the pair of electrodes which were furthest apart (190.8 cm.). *All* of these measurements are given in Table IV, V, and VI, and the only measurements excluded from the final average are those enclosed by brackets in these tables. It seems desirable to present this complete statement of the data, so that there shall be no question as to the absolute reality of the very minute effect which was measured. The final average deflections obtained from these tables can now be compared with the values that can be predicted from equation (8).[1]

(*a*) *Comparison of Deflections with Values Predicted from Equation (8).*—Equation (8) gives us for the number of coulombs of electricity, Q, sent through the external circuit when a column of a solution of alkali iodide, AI, is accelerated,

$$Q = \frac{lu}{10^7 F(R+R_e)} \left\{ I(1 - \bar{v}_{I_2} d) - n_c AI(1 - \bar{v}_{AI} d) \right\}$$

where (l) is the distance between the electrodes in centimeters, u is the final velocity in centimeters per second attained by the column of solution (equals 6.42 revolutions per second × 207.3 cm., the circumference of the wheel), F the value of the faraday in coulombs (96540), $R + R_e$ the total resistance in the circuit in ohms (equals the resistance of the solution + 1315 ohms for the galvanometer), I the atomic weight of iodine, $\bar{v}_I$ the partial specific volume of iodine in the solution, d the density of the solution, n_c the transference number of the cation, AI the molecular weight of the iodide, and $\bar{v}_{AI}$ the partial specific volume of the iodide in the

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[1] In the calculations no allowance has been made for the effect of the slight change in temperature which would be produced at the rear electrode by the compression of the liquid incident upon acceleration.

TABLE IV.

Measurements on Potassium Iodide.

Solution, 1 kilo water, 1 mol. KI, 1/100 mol I_2.
Distance between electrodes, 190.8 cm. Resistance, 1110 ohms.
Extension of spring, $5^3/_8''$ = 6.42 revolutions per second.

Date.	Original deflection in mm.	Galvanometer throw in mm.	Remarks.
May 23, 1912, A.M.........	— 3	(0.7–1.2)	Throw increased from 0.7 to 1.2 mm.
	— 3	..	Throw merged into a deflection 3–4 mm.
	— 3	0.5	Secondary, $-1^1/_2$ mm.
	..	..	Solution stirred.
	— $2^1/_2$	0.9	
	— $1^1/_2$	1.0	Difficult to distinguish from secondary of 2 more in same direction.
	0	0.9–1.0	
	0	..	Throw merged into a deflection of 4 mm.
May 23, 1912, P.M.........	13	0.8–0.9	
	9	0.9	
	9	0.7	
	7	0.9	
	12	(0.3)	Quick secondary, —7 mm.
	5	0.9	
	1	0.9	
	6	1.2	
	6	0.9	
	9	0.9	
	9	1.0	
	13	1.1	
	10	(2.0)	Continued to increase a little, galv. throw and secondary not distinguishable.
	..	..	Solution stirred.
	3	..	Throw merged into a deflection of 3 mm.
	..	..	Solution stirred.
	$3^1/_2$	0.9	Difficult to distinguish from a secondary of 4–5 mm. more in same direction.
	..	..	Solution stirred.
	3	0.9	Secondary, —2 mm.
	3	0.8	Secondary, —2 mm.
	5	1.2	Continued to increase a little.
	8	1.0	
	9	0.8	Secondary, —3 to —4 mm.
	7	0.9	Secondary, —3 mm.
Average galvanometer throw.........		0.91 mm.	

TABLE V.

Measurements on Sodium Iodide.

Solution, 1 kilo water, 1 mol NaI, 1/100 mol I_2.
Distance between electrodes, 190.8 cm. Resistance, 1370 ohms.
Extension of spring, $5^3/_8'' = 6.42$ revolutions per second.

Date.	Original deflection in mm.	Galvanometer. throw in mm.	Remarks
May 27, 1912, A.M	2	0.9	
	— 4	1.1	Difficult to distinguish from a secondary 1 more in same direction.
	— 5	(1.5)	Probably partly secondary
	— 9	1.0	Secondary, 5 mm.
	..	..	Solution stirred.
	— 3	0.7	
	— 3	1.0	
	— 2	1.0	Slight secondary in same direction.
	0	1.0	
	8		More or less permanent deflection of 12 mm.
	3	0.9	Large negative secondary.
	— 3	0.8–0.9	Large negative secondary
	.	..	Solution stirred.
	0	0.9–1.0	Large negative secondary.
	— 5	0.8	Small, slow negative secondary.
	— 6	0.9	
	1/2	0.95	Small negative secondary.
	— 2	0.9	
	— 2	1.0	
	— 1	1.0	
	0	1.0	Secondary, —1 mm.
	— 1	0.95	Slight negative secondary.
	— 3	0.9–0.95	
	— 4	0.9–0.95	
	— 3	0.9	Slight negative secondary.
	— 5	0.8	
	..	..	Solution stirred.
	— 3	0.5	Small negative secondary after wheel stopped.
	..	.	Solution stirred.
	— 3	1.0	
	— 3	0.9	
	— 2 1/2	1.0	Secondary, 0.1 mm.
May 27, 1912, P.M.........	—14	0.8	Difficult to distinguish from secondary 5–6 more in same direction.
	.		Solution stirred.
	—12	0.9	Small secondary in same direction.
	.	.	Solution stirred.
	— 9	0.8–0.9	Secondary, —1/2 mm.
	..	..	Solution stirred.
	— 4	0.95	
	..	..	Solution, stirred.
	— 4	0.9	Secondary, —3/4 mm.
	..	..	Solution stirred.
	— 9	1.0	Slight secondary in same direction.
May 28, 1912, A.M.........	—29	0.85	Followed after a pause by a secondary in same direction.
	—23	0.95	
	—22	0.95	
Average galvanometer throw.........		0.91 mm.	

TABLE VI.

Measurements on Lithium Iodide.

Solution, 1 kilo water, 1 mol LiI, 1/100 mol I_2.
Distance between electrodes, 190.8 cm. Resistance, 1900 ohms.
Extension of springs, $5^3/_8''$ = 6.42 revolutions per second.

Date.	Original deflection in mm.	Galvanometer throw in mm.	Remarks.
May 31, 1912, P.M.	—6	(8–10)	One big throw.
	—1	1.1	Secondary, $^1/_2$ mm.
	—3	1.0	
	—6	1.1	
	—6	0.95	
	—7	0.95	
	—7	0.95	
	—6	1.0	
	—5	1.0	
	—5	1.0	Slight negative secondary
	—5	0.9	Secondary, —1 mm.
	—6	0.9	Secondary, —1 mm.
	—6	1.0	Secondary, —$1^1/_2$ mm.
	—7	1.0	Secondary, —1 mm.
	—8	1.0	Secondary, —$^1/_2$ mm.
	—8	1.0	
	—8	1.0	Secondary, —$^1/_2$ mm.
	—9	1.05	
	—12	1.0	Secondary, —1 mm
	—12	0.9	
Average galvanometer throw		0.99 mm.	

solution. The following table (VII) presents the values of the above quantities used in the computations and the values of Q thus calculated. The densities, specific volumes, and transference numbers employed are transcribed from an article[1] on "The Electromotive Force Produced in Solutions by Centrifugal Action" by one of the present authors.

TABLE VII.

Solution.	l.	v.	$R + R_e$.	I.	v_{I_2}.	d.	n_C.
KI	190.8	1330	2425	126.9	0.2376	1.115	0.486
NaI	190.8	1330	2685	126.9	0.2376	1.110	0.385
LiI	190.8	1330	3215	126.9	0.2376	1.096	0.268

Solution.	AI.	v_{AI}.	Q.	Q/D.	Deflection. Calc.	Deflection. Obs.
KI	166.0	0.284	0.412×10^{-8}	0.593×10^{-8}	0.7 mm.	0.9 mm.
NaI	149.9	0.244	0.511×10^{-8}	0.559×10^{-8}	0.9 mm.	0.9 mm.
LiI	133.9	0.2605	0.557×10^{-8}	0.507×10^{-8}	1.1 mm.	1.0 mm.

In the next to the last column of the table we have put values of the expected deflection as calculated from the values of Q, making use of values for the sensitiveness of the galvanometer Q/D, obtained by interpolation from Table I for the particular resistances in series with the galvanometer. These values may be compared with the observed values as given in the last column. We feel that the agreement is within the limit of experimental error, when we consider the difficulties of rapidly estimating tenths of a small scale division. The greatest deviation is in the case of KI solution, the calculated value being 0.7 mm. and the observed value 0.9 mm. The deviation in this direction might be partly due to a tendency to estimate as 0.9 of a division anything slightly under 1 division.

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[1] Tolman, THIS JOURNAL, 33, 121 (1911).

(*b*) *Change in Galvanometer Throw with Speed of Apparatus.*—Further evidence of the correctness of our theory of accelerated conductors may be obtained from the fact that the magnitude of the galvanometer throw was found to increase with the magnitude of the acceleration. According to our theory, the galvanometer throw should be directly proportional to the final speed attained by the wheel. In the case of the *potassium iodide* solution only one isolated acceleration was made with any extension of the spring other than $5^3/_8''$. In the case of the *sodium iodide* solution, eight accelerations were made with an extension of $2^1/_4''$, corresponding to a velocity of 3.09 revolutions per second (see Table III). The average of the eight galvanometer throw for the speed 3.09 was 0.35 mm., while the average galvanometer throw for the speed 6.42 was 0.91 mm.(see Table V), figures which certainly check our theory within the experimental error.

In the case of the *lithium iodide* solution, one isolated measurement was made with a spring extension of about 8″, and nine measurements were made with a spring extension of 7″, corresponding to a velocity of 8.11 revolutions per second (see Table III). The average of the nine galvanometer throws for the speed 8.11 was 1.17 mm., while the average galvanometer throw for the speed 6.42 was 0.99 mm. (see Table VI), figures which again check our theory with the experimental error.

(*c*) *Change in Galvanometer Throw with Distance between the Electrodes.*—Further evidence of the correctness of our theory of these acceleration effects is given by the fact that the galvanometer throw became smaller when the distance between the electrodes was smaller. Both with the sodium iodide and the lithium iodide solution, accelerations were made with $5^3/_8''$ extension of the spring and the pair of electrodes which were nearest together (66.4 cm.). These measurements were not as satisfactory as the other measurements, both the "original deflection" and the "secondary deflection" being oftentimes very large. This was perhaps partly due to the fact that the two electrodes which were connected by the shortest length of conducting solution were in reality much further apart on the wheel, as will be seen from the diagram, than the pair of electrodes usually employed which were separated merely by a stopcock. This might tend to increase the difference in the conditions around the electrodes.

With the sodium iodide solution 52 accelerations were made. Owing to large "secondary deflections" or other reasons, the values of the measurements were discarded in 17 cases; the remaining 34 measurements gave an average "galvanometer throw" of 0.26 mm.

Allowing for the smaller resistance of the column of solution (515 ohms) when the electrodes nearest together (66.4 cm.) were used, it is possible to calculate the expected galvanometer throw from the value (0.91 mm.) obtained when the electrodes were furthest apart (190.8 cm.), and the resistance of the solution was 1370 ohms. The calculated value is 0.37 mm. which agrees with the above within the probable experimental error. (The change in sensitiveness of the galvanometer with resistance has been allowed for with the data given in Table I.)

With the lithium iodide solution 13 accelerations were made with the electrodes nearest together. The values of the measurements were discarded in 5 cases, the average value of the remaining 8 galvanometer throws being 0.32 mm. The resistance of the short column of LiI solution was 720 ohms.

The expected value of the galvanometer throw, calculated on the basis of a throw of 0.99 mm. with the electrodes furthest apart would have been 0.42 mm., which is again a check within the probable experimental error.

In concluding our account of this experimental work, it should be noted that when the tube of solution was replaced by a single turn of copper wire absolutely no effects were observable in the galvanometer on acceleration, showing that the effects were not of accidental origin, and that the winding upon the hub of the wheel of the flexible connecting wire introduced no error.

6. Conclusions.

The data presented in the preceding sections afford conclusive proof that potential differences are developed at the ends of a column of accelerated electrolyte, and, within the necessarily large experimental error, check the requirements of our theory of accelerated solutions. Previous to these determinations, the only work reported on accelerated electrolytes was an experiment of Colley[1] made in 1882 by dropping a tube of cadmium iodide solution. His result was also in approximate agreement with theory.

It might seem as though there were no necessity for carrying out these measurements of the very small potential differences which can be produced in accelerated solutions, since the similar electromotive forces that are produced in solutions by the action of obtainable centrifugal forces are much larger and have already been thoroughly investigated.[1] The measurements were made, however, with the view of extending such investigations to the much more difficult problem of metallic conductors where, as we shall see, the acceleration method is far better adapted than the centrifugal method. Hence it seemed desirable to obtain some preliminary experience with accelerated electrolytes and get, if possible, a check on the general theory of accelerated conductors.

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[1] Colley, *Wied. Ann.*, 17, 55 (1882).

PART II. METALLIC CONDUCTORS.

(Experimental work performed in the Chemical Laboratory of the University of California by R C. Tolman and T D Stewart)

1. Introduction.

At the present time, we have at our command much less definite information concerning the physical-chemical structure of metallic conductors than we have for electrolytes. There have, however, long been theoretical reasons for supposing that the current is carried at least in *solid* metals largely by the negative electron, and of late years there has been increasing experimental evidence in support of such a hypothesis.[2]

If this hypothesis is correct, the carrier of electricity in a metal should have a mass about 1/1800 of that of the hydrogen atom, and it should be possible to obtain evidence of its presence either by a centrifugal method, in which a measurement would be made of the difference in electrical potential between the axis and rim of a rotating metallic wheel, or by an acceleration method similar to the one which we have just described for electrolytic conductors.

The centrifugal method, which is quite successful for electrolytic conductors, is not at all well adapted for metals. In the case of rotating tubes of electrolyte, electrical connection with both the inner and outer electrodes can be made by wires which lead to central mercury cups and connection with these cups can be made to the measuring apparatus. In the case of a rotating disk of metal, however, if a wire connection be taken from the periphery to a central mercury cup, the electromotive force set up in this wire will obviously be just equal and opposite in direction to the potential difference between the periphery and axis of the disk and hence completely neutralize the desired effect.[3] For this reason it is necessary to make connection with the periphery of the wheel with some form of rubbing contact and this will itself produce large and variable electromotive forces. Experiments with a rotating aluminum disk were made by Nichols[4] who found that the variable electromotive forces produced by the contacts were relatively very large, although he was able to conclude from his experiments that the mass of the carrier of electricity in metals must at least be smaller than the mass of the hydrogen atom

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[1] Tolman, THIS JOURNAL, 33, 121 (1911).

[2] See, for example, Richardson, *Science*, 38, 57 (1913). Kraus, THIS JOURNAL, 35, 1732 (1913).

[3] In the case of the electrolyte the electromotive force set up in the wire connection is of course negligible in comparison with that set up in the tube of electrolyte.

[4] Nichols, *Physik. Z.*, 7, 640 (1906).

The acceleration method seems much more suitable for metals, and the authors have carried out measurements by this method which show that the mass of the carrier in metals is probably less than 1/200 that of the hydrogen atom The authors believe, however, that it will be quite possible to modify further the apparatus so as to detect the still smaller effects which would be produced if the carrier is really the electron with a mass 1/1800 that of the hydrogen atom

2. The Apparatus.

The accompanying photograph, Fig. 2, shows the main features of the apparatus which we employed. It consists essentially of an aluminum alloy (Macadamite) disk $11^1/_2''$ in diameter with a groove cut in the rim $^5/_8''$ wide and $^3/_4''$ deep. In this groove was wound 2407 feet of No 28 silk insulated copper wire making connection at the two ends with the insulated binding posts seen at the centre of the disk. The insulation between the wire and the disk was found to be entirely satisfactory, and the lengths of the wire, as determined by weight and by resistance, were found to be the same, showing satisfactory insulation between the different turns of wire.

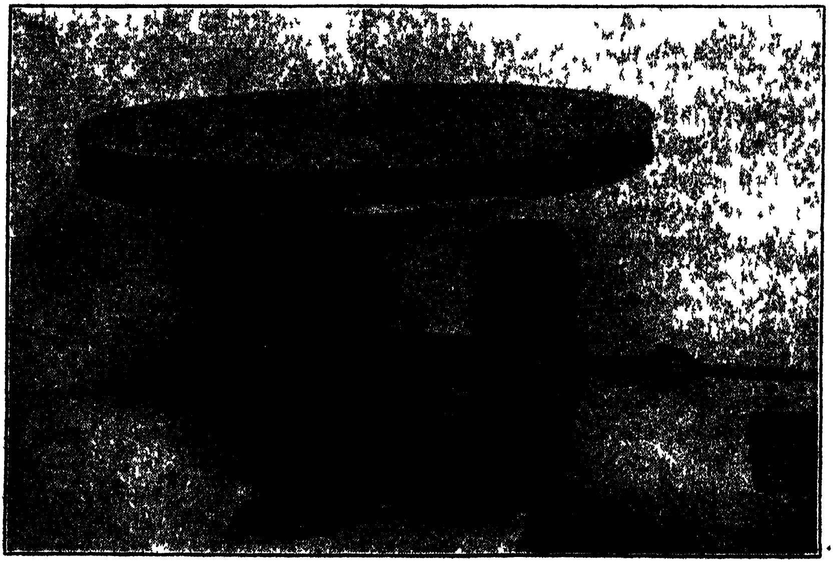

Fig 2

The disk was mounted on a vertical shaft, connected by enclosed spiral gears (ratio of 3 to 29) with the horizontal shaft carrying the pulley seen at the right of the picture. This pulley was belted direct to a two horse power motor. It was found necessary to make the pulley out of bronze since the magnetic effect of a rotating iron pulley produced large and fluctuating electromotive forces in the coil on the disk, because of the very large number of turns of wire.

A brake, not shown in the figure, was arranged for bringing the disk quickly to rest. It functioned by squeezing the rim of the wheel between leather pads and would bring the disk to rest almost instantaneously from a speed of 5000 revolutions per minute.

To measure the speed of rotation the apparatus was made to drive a magneto, which was placed about eight feet away in order to minimize magnetic disturbances. This magneto was driven by the small shaft leading off to the right of the picture. The voltage of the magneto, which was approximately proportional to the speed, was read on a voltmeter placed conveniently near to the operator of the apparatus.

For the apparently difficult problem of making, between the rotating coil and the galvanometer, an electrical connection which would not itself introduce appreciable electromotive forces, a surprisingly simple and satisfactory solution was eventually found. The connection was made through fine silk insulated wires which led directly up from the binding posts and were allowed to twist up when the apparatus started. In order to allow for the shortening produced by the twisting, the wires were led over a pulley providing sufficient slack which was kept tight by a small weight The wires went through a hole in the ceiling to the ceiling of the room above, and this allowed for enough twisting so that two or three runs could be made before the wires broke. The insulation between the twisted wires was found to be entirely satisfactory, and with the galvanometer employed we could not find that any electromotive force was produced by the twisting.

The galvanometer was connected directly in series with the rotating coil through the above connections. It was a Leeds and Northrup high sensibility galvanometer, having a resistance of 36 ohms and was used without damping coils. The galvanometer was mounted on concrete masonry and showed no observable deflections when directly short circuited. Its sensitiveness as a ballistic galvanometer was found by discharging the secondary of a standard solenoid through it, having in the circuit the same total resistance as with the coil of wire on the disk. The distance from the galvanometer mirror to the scale was about fifty inches and the sensitiveness approximately 2.1×10^{-8} coulombs per 1 mm. throw.

3. The Experimental Work.

The experiments consisted in bringing the apparatus to a high speed of rotation, suddenly stopping the disk and observing whether there was any pulse of electricity through the galvanometer.

Even when the wheel was entirely at rest the galvanometer was usually found to be giving small and variable deflections. These deflections were mostly not very rapid, although sometimes there would be sudden jumps, the total range of deflection usually being inside of 1 mm., and often less for long periods of time. It was found that these variable deflections were apparently caused by variations in the magnetic flux through the large number of turns of wire in our coil, these variations being due to nearness to the disturbances of the city of Berkeley. By going about a mile up the canyon back of the university and setting up the same galvanomteer it was found that these effects disappeared. The deflections were not large enough to interfere seriously with our experiments at their present stage of accuracy, but would have to be eliminated before further progress could be made.

Besides these deflections, which were produced by fluctuations in magnetic field, it was found that the slight tipping which could be given to the disk because of the natural looseness of the vertical shaft in its bearings would cut enough lines of force to produce a galvanometer throw of about 5 mm. Even putting on the brake when the wheel was entirely stationary would usually produce tipping enough to cause perhaps as much as a millimeter throw. For this reason we could not expect the galvanometer to remain absolutely stationary when the rotation of the wheel was stopped by the brake, and in fact on stopping the wheel we obtained throws all the way from zero up to 3 or 4 mm. Before further progress can be made these accidental effects will have to be eliminated.

4. Results.

From our experiments, however, we think it pretty safe to conclude that on reducing the speed from the neighborhood of 5000 revolutions per minute to zero there was no systematic galvanometer throw greater than 1 mm. which would correspond to 2.1×10^{-8} coulombs.

Consider now equation (8), which connects the quantity of electricity delivered, on accelerating an electrolytic conductor, with the total change in velocity, the length of the conductor, the equivalent weights of the carriers, etc. For the case of metallic conductors we may consider that the only mobile carrier is the electron, and may at least temporarily assume that its partial specific volume is small enough to be negligible, which will give the equation the simple form

$$Q = \frac{(l)u}{10^7 F\,(R + R_e)}\,m \qquad (9)$$

where m is the equivalent weight of the electron. Putting $Q = 2.1 \times 10^{-8}$ coulombs (which corresponds to a galvanometer throw of 1 mm.), $l =$ 73500 cm. (the total length of the wire), $u = 7100$ cm./sec., (the rim velocity at 5000 r. p. m.), and $R + R_e = 136$ ohms, the total resistance of the circuit, we obtain for *m* the approximate value 0.005, showing that the mass of the carrier in metals is probably less than 1/200 that of the hydrogen atom.

5. Conclusions.

We believe that these experiments have set a limit for the mass of the carrier in metals considerably lower than any previous experimental work.[1] We see, moreover, no insuperable difficulties in carrying the sensitiveness of our method to a point where the electron, if it really is the carrier of electricity in metals, with a mass 1/1800 that of the hydrogen atom, should produce an appreciable effect. One of our main purposes in giving this brief description of our work on metallic conductors is the hope that we may be able to obtain funds for carrying this research to completion, a consummation which for many years has been the desire of one of the present authors.[2]

A tenfold increase in the accuracy of the observations would apparently be sufficient for the desired purpose, and it seems probable that this could be obtained if we could eliminate the accidental effects produced by uncontrollable variations in the earth's magnetic field and those produced by the small tipping of the disk which unavoidably occurs when the brake is applied. Probably the best way to accomplish this result will be to try to construct efficient screens for cutting out the earth's magnetic field from the apparatus. With the help of such a magnetic screen and some increase in the sensitiveness of the apparatus, which could be obtained by increasing the length of wire on the disk and its rim velocity, as well as obtaining a more sensitive galvanometer arrangement, it should be quite possible to solve the problem.

BERKELEY, CAL.

ON THE TRANSITION TEMPERATURES OF THE HYDRATES OF SODIUM CARBONATE AS FIXED POINTS IN THERMOMETRY.

BY THEODORE W. RICHARDS AND AUGUSTUS H FISKE

Received December 15, 1913

Recent investigations conducted in this laboratory, and confirmed elsewhere, have shown that the transition temperatures of hydrated crystalline salts provide excellent means for fixing definite points upon the thermometric scale.[1] The transition temperature of the dekahydrate of sodium sulfate at 32.383°[2] was first selected, for many reasons; and it has proved to be the most convenient of any as yet studied. Although sodium sulfate is thus to be preferred if only a single point near the ordinary temperature of the room is sought, obviously the knowledge of other points would be desirable. Accordingly, a number of other substances have been investigated with regard to their suitability for the purpose.

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[1] As far as we know, the only quantitative experiments reported in the literature are those of Nichols of which we have already spoken. Maxwell ["Treatise on Electricity and Magnetism," 3d edition (1892), Vol. II, et seq.] and Lodge ["Modern Views of Electricity" 3rd edition (1907), p. 89] have both attempted, without success, to obtain effects dependent on the mechanical momentum which might be associated with the passage of a current of electricity, but give no figures as to the sensitiveness of their methods.

[2] See Tolman, *Science*, 37, 192 (1913).

Among the salts suggested in the second Harvard paper (1899) was sodium carbonate. At that time little was known concerning the transition temperatures of the various hydrates of this salt; accordingly, a preliminary determination of one of the points was made, and it was shown that satisfactory constancy was attainable.[3] The intention was to study this and other points more carefully, but soon afterwards several investigations, especially those by Epple,[4] Ketner,[5] and Wells and McAdam,[6] largely covered the ground. These researches, especially the last, have shown clearly that the stable hydrates are the following: between − 2.1° and +32.0°, the dekahydrate; between 32.0° and 35.4°, the heptahydrate; and above 35.4°, the monohydrate. Wells and McAdam found also that the transition between the dekahydrate and the monohydrate is 32.96°, and their diagram shows very clearly the situation.

Although the work of Wells and McAdam was very carefully done, it seems desirable to verify these points upon as many accurate instruments as possible, and also to determine how well fitted they may be for the standardizing of thermometers. If they are easily reproduced, the three transition temperatures would form an exceedingly useful means of calibrating a Beckmann instrument, since they cover three and one-third degrees, with an intermediate point. The present paper is concerned with the redetermination of the lowest of the three points.

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[1] T. W. Richards, *Am. J. Sci.*, [4] **6**, 201 (1898); Richards and Churchill, *Proc. Am. Acad.*, **34**, 277 (1899); Richards and Wells, *Ibid.*, **38**, 435 (1906); *Ibid.*, **38**, 431 (1902); Richards and Wrede, *Ibid.*, **43**, 343 (1907); Richards and Kelley, *Ibid.*, **47**, 171 (1911). Four of these papers are to be found in full in the *Z. physik Chem.*, the references being respectively, **26**, 690 (1898); **28**, 313 (1899); **43**, 465 (1903); **61**, 313 (1908). The work on manganese chloride was finished by Dr. Wrede and one of us at the University of Berlin. The sixth paper appeared also in THIS JOURNAL, **33**, 847 (1911). Jeannel (*Compt. rend.*, **62**, 834 (1866)) suggested long ago the use of a transition point of hydrated sodium acetate for testing and standardizing thermometers, but no one seems ever to have followed up the suggestion or to have actually used it in this way. The fact that such a suggestion concerning any crystalline salt had been made before 1898 has been unknown to the present authors until now. We are indebted to Professor W. Lash Miller for his having called our attention to it.

[2] Dickinson and Mueller (*C. A.*, **2**, 7 (1908)) found 32.384°, confirming as nearly as could be expected the value found in this laboratory.

[3] Through a typographical error the initial hydrate was stated to contain 10 H_2O instead of 7 H_2O (*Proc. Am. Acad.*, **34**, 278 (1909)), but this error was eliminated when the paper was reprinted in the *Zeitschrift für physikalische Chemie*, two months later.

[4] Inaug. diss., Heidelberg, 1899.

[5] *Z. physik. Chem.*, **39**, 645 (1902).

[6] THIS JOURNAL, **29**, 721 (1907).

Purification of sodium carbonate is conveniently conducted by recrystallization. The purest "chemically pure" material of commerce was recrystallized ten times, the transition temperature of each successive group of crystals being taken; the purification was continued until no further change occurred in the transition temperature. The crystallization was conducted by cooling from about 40° to 10°; and centrifugal draining helped to eliminate the mother liquor. During the last three crystallizations the substance came into contact only with silver or platinum.

Pure sodium carbonate is not easily kept without deterioration, because it, of course, attracts any trace of hydrochloric or sulfuric or even carbonic acid which may be in the air, either through leakage from stoppers of the laboratory reagent bottles or from the products of combustion of illuminating gas. If the best results are to be obtained from the salt, it must be protected with the utmost care, or better, used at once. We have often found that material even preserved over lime or potash for as short a time as twenty-four hours, may change several thousandths of a degree as to its transition temperature, unless the desiccator is well sealed. One of the samples (F), having been kept under a bell-jar not perfectly tight, had its transition point lowered as much as 0.02° in three weeks by impurities taken from the laboratory air. That the salt will keep perfectly pure, when properly guarded, is proved by the very constant results obtained from the purest samples, to be recounted in the following pages.

The water of crystallization in the various phases of the salt was determined by titrating weighed amounts of the roughly pulverized crystals (dried in air until just to the point of efflorescing) by means of half normal hydrochloric acid, methyl orange being used as the indicator. The substance employed in the final determinations showed an average molecular weight of 281, the theoretical molecular weight of $Na_2CO_310H_2O$ being approximately 286. After these crystals had been entirely transformed at 32.02° into the other phase in equilibrium at that temperature, the crystals constituting this new phase were separated from the supernatant mother liquor, pressed on warm filter paper in a warm room at about this temperature and analyzed as before. The resulting crystals, when freshly prepared, were found to have a molecular weight averaging 234, leaving no doubt that the phase in question was the heptahydrate, which has a theoretical molecular weight of 238. Pursuing the same quest further, we heated the substance for some time above 40°, when a new phase appeared which was found, after separation of the mother liquor, to have the molecular weight of 124—thus being without question the monohydrate, which has this theoretical value. All of these phases, on standing, in a desiccator over a large excess of concentrated sulfuric acid for three or four weeks, give a substance having a molecular weight below 107, showing that under these conditions the water is practically all removed (Na_2CO_3 = 106). These conclusions, except the last, all correspond with the statements of Wells and McAdam.

The successive products of the first five recrystallizations, made from distilled water in porcelain dishes, were all prepared before April 15, 1911, portions of each having been saved for the study of their transition temperatures. After an intermission of a week, two more crystallizations in porcelain were made, and then all of the seven samples were carefully compared as to their transition points.

The preliminary determination of the constancy of the transition temperature was made by means of a sensitive Beckmann thermometer in an apparatus essentially like the Beckmann freezing-point apparatus, as indicated in previous papers. The large test-tube containing the salt was surrounded by an air jacket, and this latter was immersed in a water bath, kept about 0.3° higher than the temperature to be observed by means of a suitable electric coil. The transition point showed a slight and steadily decreasing rise with increasing purity, until sample *E* was reached. Two subsequent recrystallizations made no further change in this value—apparently this was the purest salt which could be obtained by recrystallization in porcelain. In the meantime the crystallization was being carried further, from the purest water, in platinum; with this product another constant point 0.001° or 0.002° higher than the preceding, was soon reached. This seemed to be the maximum, and therefore the true transition point of the really pure substance.

After the ninth product (sample *I*) had had its transition point redetermined several times over a period of several weeks, it was recrystallized once more; and because the corrected reading of the Beckmann thermometer at the transition point of this material gave almost exactly the same value as the preceding, the final determination of the transition temperature was made as soon as possible.

Before the final readings are presented, a tabulated statement of the preceding results may be given; it is of interest as indicating the exact measure of the impurity eliminated in each of the successive steps. One may note that the Beckmann readings needed correction for the pressure (0.002° per centimeter of barometer) and for the temperature of the emergent column (0.001° per degree Centigrade). The comparison of the observed values in the second column and the corrected values in the sixth is not without interest, because it shows how erroneous may be the reading of a sensitive mercury thermometer not thus corrected. The true temperature given in the last column was obtained by adding the quantity

31.628 to each of the readings of the Beckmann thermometer; this quantity was found in the final experiments to be recorded further on

Date 1911.	Material of dish	Observed	Bar	Cor pres	$t°$ of emergent column	Emergent column cor rected to 25°	True temperature
Apr. 25	Porcelain	A = 0 309	764 0	0 308	27	0 306	31 934
Apr 27	"	B = 0 352	771 0	0 350	28	0 347	31 975
Apr 28	"	C = 0 370	760 0	0 370	28	0 367	31 995
Apr 29	"	D = 0 380	765 0	0 379	24	0 380	32 008
Apr 15	"	E = 0 382	760 0	0 382	19	0 388	32 016
Apr 24	"	G = 0 382	758 0	0 382	19	0 388	32 016
Apr 24	Platinum	H = 0 388	763 0	0 387	23	0 389	32 017
Apr 25	"	I = 0 389	764 0	0 388	23	0 390	32 018
		0 395	758 0	0 395	30	0 390	
May 12	"	0 392	757 0	0 393	28	0 390	
May 13	"	J = 0 394	757 0	0 395	30	0 390	32 017
May 13	"	0 393	761 0	0 393	29	0 389	
May 15	"	K = 0 389	761 0	0 389	25	0 389	

Complete constancy having thus been obtained, the final temperature readings were made on very exact Baudin thermometers, 15200 and 15276, which have already been described in Harvard papers.[1] Every precaution was taken with the observation, which was made with a very accurate Geneva cathetometer, the thermometers were fixed in a perfectly vertical position, and many readings were made, both from the front and through the back of the stems. Thanks are due to Dr. A. W. Rowe and Dr. G. L. Kelley for their help in making additional readings of these crucial observations. The usual corrections for calibration, internal pressure, external pressure, the fundamental interval and the average ice point (likewise thus corrected) were applied, as well as further correction for the emergent column. This last was computed in the usual way, and is probably correct to within 0.001° or 0.002°. The final results are tabulated below.

After these determinations, the original Beckmann thermometer was again inserted into the mixture; it then indicated a temperature 0.001° lower than before—an almost negligible difference, perhaps due to impurities taken from the glass and the air during the several hours needed for the exact thermometric readings.

Thus, the transition from the dekahydrate of sodium carbonate to the heptahydrate was found to take place at 32.017° This value is near the reading (32.00°) found by Wells and McAdam, but decidedly higher than the result of Ketner (31.85°). The latter evidently had been less successful in purifying his substances; for impurities usually lower the transition temperature.

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[1] *Proc. Am Acad*, **38**, 434 (1902); *Z. physik Chem*. **43**, 467 (1903)

THE TRANSITION TEMPERATURE OF SODIUM CARBONATE: DEKAHYDRATE-HEPTAHYDRATE.

Designation of thermometer.	15276.	15200.
Observed reading...	32.187	32.257
Cor. for calibration...	+ 0 006	— 0.005
Cor. for interior pressure...	+ 0.056	+ 0.038
Cor. for exterior pressure...	+ 0.001	+ 0.001
Cor. for fundamental interval...	+ 0.001	+ 0.022
Cor. for corrected ice point...	— 0.154	— 0.212
Cor. for emergent thread[1]...	+ 0.023	+ 0.020
	32.120	32.121
Cor. to hydrogen scale...	— 0.104	— 0.104
Final value...	32.016	32.017

Although this point is quite sufficiently sharp to serve as a means of standardizing thermometers, it is probable that the other two points (namely, that involving the dekahydrate and monohydrate, and that involving the heptahydrate and monohydrate) are even sharper and more easily maintained, since as a rule, other things being equal, an increased latent heat of transition means increased precision. With any given salt, the larger the number of molecules of water lost in transition, the larger will usually be the latent heat of the change. The transition from the dekahydrate to the heptahydrate observed in the experiment just described involves a loss of only three molecules of water, whereas that from the heptahydrate to the monohydrate means a loss of twice, and that from the dekahydrate to the monohydrate three times as much.

Summary.

In this paper one of the transition temperatures of hydrated sodium carbonate, namely, that between the dekahydrate and the heptahydrate, has been carefully determined with standard instruments, and found to be 32.017° on the hydrogen scale, a value not very much above that of Wells and McAdam, who found 32.00°. Incidentally, the hydrates stable at various temperatures have been analyzed and have been found to correspond to the statements of these investigators. It is shown, moreover, that all of the hydrates lose water easily at ordinary temperatures into air dried by concentrated sulfuric acid, leaving the salt essentially anhydrous, whereas some previous experimenters have thought that one molecule of water still remained under these circumstances.

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[1] Twenty-four degrees of thermometer 15276 and twenty-one degrees of thermometer 15200 were exposed to the room temperature of 26.0°

THE COMPRESSIBILITY OF ICE.

By Theodore W. Richards and Clarence L. Speyers.[1]

Received January 29, 1914.

This investigation was conducted during the year 1909, and a preliminary report, giving the results but no details, was published in the Year-Book of the Carnegie Institution of Washington for 1910.[2] In view of the fact that the compressibility of ice is a very interesting property from many points of view, and also because no other actual experimental determination of this constant seems ever to have been made, a more complete discussion of the data and results may be expedient.

The experimental details have already been so carefully described in previous papers from the Chemical Laboratory of Harvard College that further description is perhaps unnecessary. Of course it was imperative to work at a constant temperature so far below zero that the ice would not melt under pressure. This temperature (−7.03°) was maintained by packing the compression apparatus in ice, bathed in a dilute solution of common salt, into which portions of a more concentrated solution were stirred from time to time as the ice in the bath melted. The glass piezometer was first wholly filled with mercury, and subjected to carefully measured, gradually increasing pressures; afterwards it was partly filled with ice (which of course displaced an equal volume of mercury), and again subjected to quantitative compression. The determination of volume was effected by allowing the mercury to make contact with a very finely pointed platinum wire in a capillary tube, changes in volume being determined and measured by weighed globules of mercury added through the capillary. From the curves indicating the relations of added pressure to added mercury in the two cases, the difference between the compressibility of mercury and of ice is very simply calculated. The compression of the apparatus, occurring equally in the two series, is entirely eliminated from the result.

The form of piezometer was essentially that indicated by the diagram taken from a previous paper.[3] Dilute alcohol was used in the capillary above the mercury, instead of water as usual. It was found that in this apparatus in two successive and entirely distinct trials with mercury alone in the apparatus, a variation in pressure of 398 megabars[4] corresponded to 0.365 gram of mercury, and 416.5 megabars corresponded to 0.389 gram of mercury. Evidently then on the average 400 megabars correspond with 0.370 gram of added mercury. These determinations, which took place at —7.03°, were verified by two determinations at higher temperatures. The corresponding values for 0° and 20° were, respectively, 0.378 and 0.398. By extrapolating these values about the same result (0.373) is obtained as the average given above, so that (rating each determination as of equal weight) 0.371 may safely be taken as the mercury-constant of the apparatus. The pressure gauge was very carefully verified by reference to an absolute standard.

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[1] This paper was written after the death of Dr. Speyers. The experiments were carried out by the two authors in collaboration.

[2] Year Book, *Carnegie Institution of Washington*, 9, 221 (1910)

[3] This Journal, 34, 975 (1912).

[4] The megabar is the "atmosphere" of the c g. s system, being the pressure of one million dynes per square centimeter. It is about 0.987 ordinary atmosphere See This Journal, 26, 4081 (1904). This standard of pressure has recently been adopted by the Blue Hill Observatory.

Into the apparatus thus standardized, ice was introduced in two ways. In the first place the solid was frozen as a hollow adherent cylinder in the inside of the piezometer, this having been filled with pure boiled, air-free water and packed in a mild freezing mixture. When about half of the water had been frozen, the remainder was poured out, and by carefully weighing the amount of ice clinging to the tube was determined and found to be 14.779 grams (in vacuum). While the apparatus was still packed in the freezing mixture, it was filled with cold mercury and the stopper adjusted with all the usual precautions so often described in previous papers. It was then subjected to quantitative compression at —7.03°, and the amount of mercury which must be added for 400 megabars' increase of pressure (between 100 and 500 as before) was found to be 1.079 grams, or 0.708 more than when the mercury alone was in the apparatus.

All this was done in warm weather, during the month of June, 1909. For fear that the clinging of the ring of ice to the glass piezometer might interfere with the exact determination of the compressibility, it seemed highly desirable that a free cylinder of ice also should be compressed in the same apparatus, but during the warm weather this was not easily feasible because of the melting of the ice during the weighing and transference. In the month of December, following, however, the confirmatory experiment was actually carried out in a very cold room. A cylinder of ice weighing 9.475 grams in vacuum was compressed in the same glass piezometer in the usual fashion, and the total amount of mercury added for 400 megabars was found to be 0.815 gram. Subtracting the change when mercury alone is in the receptacle, 0.444 is obtained as the difference between the mercury added in the two cases over this range of pressure. From the June experiment we should conclude that the introduction of 10 grams of ice into the vessel would cause an added mercury value of 0.479, and from the December experiment that 10 grams would produce a change of 0.470. Evidently the two determinations are essentially concordant and from their average the compressibility of ice is easily calculated by substitution in the usual equation so often used in previous work:[1]

$$\beta_{100-500} = \frac{0.474 \times 0.918}{13.64^2 \times 10 \times 400} + 0.00000398 = 0.00000120.$$

The deviation of each single result from the mean is less than 1%, which is as good an outcome as could be expected considering the difficulty of the problem.

Attention should be called also to the fact that the isotherms plotted from the observations showed but little curvature—indicating that the change in the compressibility of ice with increasing pressure is not large. The average compressibility of between 300 and 500 is probably not over 3% less than that between 100 and 300 megabars. Thus in the first experiment the change of pressure from 85 to 306 megabars needed an addition of 0.5970 gram of mercury, while the further rise of pressure to 500 megabars needed the almost proportional amount, 0.5140 gram more.

The compressibility of ice, 0.0000120, as thus found at 7.03°, appears, as has been said, to be the only value for this constant which has ever been found by direct experiment. It is about one quarter of the compressibility of water at neighboring temperatures, about five times the compressibility of glass, and somewhat less than that of metallic sodium. Bridgman, in his important and interesting work upon the various forms of ice, calculated by a somewhat elaborate thermodynamic treatment the compressibility of common ice (Ice I) at 0° as 0.000036, a value three times as large as that found in these experiments. Higher pressures yielded lower results, but not correspondingly low. He admits, however, that the figures are not very trustworthy. For Ice VI, a less bulky form, he determined the compressibility at pressures above 6500 atmospheres and at temperatures above 0°, finding it to vary from 0.0000055 to 0.0000037.[3] These values seem to be much more in accord with the present work than the result of his calculation, because Ice VI at high pressures might be supposed to have a compressibility about this much smaller than Ice I. Possibly the compressibility of common ice has an abnormally high temperature coefficient which might explain a part of the discrepancy.[4]

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[1] *Loc. cit.*, p. 980. See also Stahler, *Arbeitsmethoden*, 3, 246–61 (1912). The value 0.00000398 is the compressibility of mercury over this range as computed from Bridgman's results together with some as yet unpublished results of Richards and Shipley. The preliminary adoption of this value is the reason for the fact that the values for ice given in this paper are slightly larger than in the preliminary publication

[2] This is the density of mercury under 500 megabars' pressure at —7°.

[3] Bridgman, *Proc. Am. Acad.*, 47, 536 (1912). A later calculation gives 0.000045. Bridgman, *Ibid.*, 48, 362 (1912).

[4] Bridgman's computation of the compressibility of common ice is to be found in

It should be noted that Bridgman's method of experimentation, while admirably adapted for work under high pressures and constituting a really epoch-making contribution to this kind of work, is not particularly adapted to accurate work under comparatively low pressures, such as are considered in the present discussion. In view of the fact that work precisely similar to this present research, carried out with other solids in the Chemical Laboratory of Harvard College, has yielded results admirably concordant with the other most satisfactory work upon compressibility (taking into account the modern value of the compressibility of mercury); and also in view of the fact that our work upon liquids also agrees with Bridgman's, insofar as they are comparable, one can hardly escape the conclusion that the compressibility of ice is really as low as that found here. Incidentally it may be stated that the great apparent disagreement between certain of our results on liquids and the best work of others, as suspected by Bridgman,[1] really does not exist. In making the comparison, he overlooked the fact that our values are all given between 100 and 500 atmospheres, and therefore should not be immediately compared with the work of others over the whole range between the atmospheric pressure and 500 atmospheres.

In conclusion, it is a pleasure to acknowledge our indebtedness to the Carnegie Institution of Washington for generous pecuniary assistance in the conduct of this investigation.

Summary.

The compressibility of ice between 100 and 500 megabars is found to be 0.0000120 at —7.03° C., or about one-quarter of the compressibility of water at neighboring temperatures. It is found not to decrease remarkably as the pressure increases. This is probably the first direct determination of the compressibility of common ice which has ever been made. The difference between the low result and the higher value obtained by Bridgman through indirect calculation is probably due, at least, in part, to the existence of a large temperature coefficient.

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Proc. Am. Acad, 47, 473 (1912). After the present paper had been sent to the press, upon having his attention called to its contents, he was able to verify the above prediction that the compressibility of common ice probably has an abnormally high temperature coefficient. With the help of his and other data, he has calculated that the average compressibility of ice between the zero of pressure and the melting pressure would be 0.000033 at 0°, 0.000023 at —5°, 0.000021 at —7°, 0.000019 at —10°, 0.000018 at —15°. The compressibility at —7° is still found to be higher than that given in the present paper, but nevertheless the agreement is much better than that of Bridgman's published results. He agrees with me in thinking that the remainder of the discrepancy may possibly be due to a considerable softening of the ice just before melting. This point is one of great interest, and will receive further experimental study here.

[1] *Proc. Am. Acad.*, 49, 48, 74.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OREGON AGRICULTURAL EXPERIMENT STATION.]

THE REACTION BETWEEN SULFUR AND CALCIUM HYDROXIDE IN AQUEOUS SOLUTION.

BY HERMAN V TARTAR

Received December 25, 1913

Introduction.

In a previous paper[1] reference was made to the commercial use of the reaction between calcium hydroxide and sulfur in the manufacture of the "lime-sulfur" spray, an insecticide now in wide general use. At that time, a résumé was also given of the literature on this and the analogous reactions of the alkali metals

The particular difficulty which presented itself in the study of the reaction between sulfur and calcium hydroxide was the easy decomposition of the calcium thiosulfate formed, into calcium sulfite and free sulfur. This decomposition obscures the primary reaction which takes place. Experiments, similar to those used in previous work,[1] were tried and it was found practically impossible to combine even small amounts of calcium hydroxide and sulfur in heated aqueous solutions without some decomposition of the thiosulfate produced. This decomposition occurs at temperatures much below 100°. After some more or less unsuccessful work had been done along this line, it was decided to attack the problem from a different standpoint. This will be explained in what follows.

Experimental.

The analytical methods employed were the same as used in former work.[2] The meaning of the coined terms, "sulfide" sulfur and "polysulfide" sulfur used here, in discussing the kinds of polysulfides, is the same as that given in an earlier paper.[3] It is unnecessary to repeat the explanation at this time.

The sulfur used was purified by recrystallization from pure carbon disulfide in such a manner that a fine crystal-meal was obtained. This was pressed free from the mother liquor and thoroughly dried at a gentle heat. It was finely ground in a mortar and sifted through an 80-mesh sieve just before using. The calcium oxide used in making the hydroxide was prepared by heating a sample of "J. T. Baker's Analyzed, C. P." calcium carbonate in a muffle furnace until it was completely converted into the oxide. The distilled water had been recently boiled to expel oxygen and carbon dioxide.

Two different solutions, each containing mixtures of calcium tetrasulfide, pentasulfide, and thiosulfate in different amounts, were prepared by boiling calcium hydroxide and sulfur in water. In each case, the sulfur was used in slight excess and the boiling continued for more than an hour. For convenience, these solutions are designated as solutions A and B. The analyses of a 20 cc. aliquot portion of solution A and a 25 cc. aliquot portion of solution B, are given in Table I.

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[1] THIS JOURNAL, 35, 1741 (1913).

[2] *Jour. Ind. Eng. Chem.*, 2, 27 (1910); THIS JOURNAL, 35, 1741 (1913).

[3] *Jour. Ind. Eng. Chem.*, 2, 27 (1910).

TABLE I.—COMPOSITION OF ALIQUOTS OF SOLUTIONS MADE BY BOILING CALCIUM HYDROXIDE AND SULFUR IN WATER.

Sample.	"Sulfide" sulfur, g.	"Polysulfide" sulfur, g.	Thiosulfate sulfur, g.	Total calcium, g. (Calculated as CaO.)	Free calcium hydroxide, g.	Sulfur combined as sulfite and sulfate, g.
20 cc. aliquot sol. A..	1 256	4 714	0.360	2 56	none	none
25 cc. aliquot sol. B..	0 866	3.178	0.936	2 42	none	none

A 20 cc. aliquot part of solution A was transferred to a liter volumetric flask containing 800 cc. of an almost saturated solution of calcium hydroxide. The flask was then connected to a hydrogen generator and pure hydrogen passed in until all the air had been expelled, in order to prevent any oxidation of the polysulfide to thiosulfate. After the removal of the air, the body of the flask was almost wholly immersed in water which was maintained at a temperature near 70°. The flask was kept in the water at this temperature for over two hours. During this time, it was gently shaken twice and a continuous stream of hydrogen passed in. Finally, the solution was allowed to cool, made up to 1000 cc. volume, and analyzed. For results see Expt. 1, Table II.

A second experiment, which was simply a duplicate of Experiment 1, was carried out. The results are also given in Table II.

In the third experiment a 25 cc. aliquot part of solution B was transferred to a half-liter volumetric flask containing 450 cc. of an almost saturated solution of calcium hydroxide. The flask was then handled in exactly the same manner as in Expt: 1, and the solution finally made to 500 cc. volume. The analytical data are given in Table II.

A duplicate of Experiment 3 was performed and the results obtained are given as Expt. 4 in the following table:

TABLE II.—COMPOSITION OF ALIQUOTS CONTAINING MIXTURES OF CALCIUM TETRASULFIDE AND PENTASULFIDE AFTER BEING HEATED IN SOLUTIONS CONTAINING EXCESS OF CALCIUM HYDROXIDE.

	"Sulfide" sulfur, g.	"Polysulfide" sulfur, g.	Thiosulfate sulfur, g.	Sulfate and sulfite sulfur, g.	Free calcium hydroxide, g.
Expt. 1..	1 456	4.312	0.520	none	present in excess
Expt. 2..	1.467	4.286	0.510	none	present in excess
Expt. 3...	0.977	2.960	1.030	none	present in excess
Expt. 4....	0.981	2.919	1.025	none	present in excess

A fifth experiment was made in the following manner: Exactly 41.38 g. of calcium hydroxide (prepared by slaking 31.32 g. of calcium oxide with water) were placed in a Jena glass flask, 2 liters capacity. To this were added 59.4 g. of sulfur, which had been thoroughly wetted, and enough distilled water to make the volume somewhat greater than 500 cc. The flask was then connected to a hydrogen generator as in the preceding experiments. The mixture of calcium hydroxide, sulfur and water was then heated to boiling and let boil briskly for 40 minutes, when the combination of the calcium hydroxide and sulfur seemed to be complete. During this time the flask was frequently shaken and a continuous stream of hydrogen passed in. The flask was next disconnected and the hot solution obtained was filtered quickly through a glass wool plug into a liter volumetric flask, cooled, made up to volume and analyzed. The results are given in Table III.

A duplicate of the preceding experiment was made and the results are recorded in Table III as Expt. 6.

TABLE III.—COMPOSITION OF SOLUTIONS OBTAINED BY BOILING CALCIUM HYDROXIDE AND SULFUR IN WATER

	"Sulfide" sulfur, g.	"Polysulfide" sulfur, g	Thiosulfate sulfur, g	Total calcium g (Calculated as CaO)	Free calcium hydroxide, g
Expt. 5	11.52	35.56	11.50	30.15	none
Expt 6	11.55	35.41	11.49	30.27	none

Discussion of Results.

It will be noted that in the two solutions whose composition is given in Table I, the "polysulfide" sulfur is more than three times greater than that of the "sulfide" sulfur. If the polysulfide present were simply the tetrasulfide (CaS_4) it would be exactly three times greater. Evidently, the solutions both contain a mixture of calcium tetrasulfide and pentasulfide (CaS_5).

The data given in Table II show that the "polysulfide" sulfur is, considering the experimental error of analysis, three times greater than the "sulfide" sulfur, indicating that the polysulfide present is the tetrasulfide. Since there was an excess of calcium hydroxide in each of these solutions, *it is evident that calcium tetrasulfide is the lowest polysulfide formed when calcium hydroxide and sulfur react in aqueous solution.*

Comparing the results given in Tables I and II, it will be seen that in Table II there has been an increase in the amounts of both the "sulfide" sulfur and the sulfur combined as thiosulfate. In each of the experiments, these forms of combined sulfur increased in equal amounts. The data presented show that the *"polysulfide" sulfur in the aliquot parts from solutions A and B, which was in excess of that required to form the tetrasulfide of the calcium combined as polysulfide, has reacted in Experiments 1, 2, 3 and 4 with more calcium hydroxide.* The results from the experiments just enumerated also show that the primary reaction between calcium hydroxide and sulfur takes place as represented by the following equation:

$$3Ca(OH)_2 + 10S \longrightarrow 2CaS_4 + CaS_2O_3 + 3H_2O$$

This reaction is analogous to that occurring with potassium hydroxide and sulfur[1] except that with the potassium hydroxide the trisulfide (K_2S_3) is formed.

In Experiments 5 and 6 the calcium hydroxide and sulfur were used in amounts proportionate to those required in the equation given in the preceding paragraph. The analytical results show that there was but a slight loss of calcium and sulfur due to the formation of the more insoluble calcium sulfite. Since there was no uncombined calcium hydroxide present, all of this substance had reacted with the sulfur. This fact and the general relationships of the amounts of the different forms of combined sulfur with each other, confirm the conclusions drawn from the preceding experiments.

In solutions A and B where an excess of sulfur was used in preparation, some calcium pentasulfide was present. This justifies the conclusion that a secondary reaction took place in which sulfur combined with the tetrasulfide to form pentasulfide.

In conclusion, it may be well to state that a discussion of the commercial application of the results here reported, will soon be presented for publication in the *Journal of Industrial and Engineering Chemistry.*

Summary.

1. The primary reaction between calcium hydroxide and sulfur in heated aqueous solution takes place as represented by the following equation:

$$3Ca(OH)_2 + 10S \longrightarrow 2CaS_4 + CaS_2O_3 + 3H_2O$$

2. When sulfur is used in excess, a secondary reaction occurs in which it combines with the tetrasulfide to form pentasulfide.

CORVALLIS, OREGON.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

SOME PHYSICAL PROPERTIES AND THE ANALYSIS OF TERNARY MIXTURES OF TOLUENE, CARBON TETRACHLORIDE AND ETHYLENE BROMIDE.

BY JOHN F. W. SCHULZE.

Received December 20, 1913.

The literature of ternary systems appears to contain only two[2] cases in which unknown ternary mixtures of organic substances have been analyzed. Schreinemakers,[1] in connection with his work on the system phenol–water–aniline, used an analytical method which was purely chemical. The other case is in the work of Barrell, Thomas, and Young,[2] who resorted to the laborious and inexact method of fractional distillation to determine the unknown composition of certain ternary mixtures,

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[1] *Loc. cit.*

[2] After this communication had been sent to the editor my attention was called to a case in which the composition of certain ternary mixtures was ascertained by determining their physical properties. Shinkichi Horiba has, namely, analyzed mixtures of water, ethyl alcohol, and ethyl ether by determining their specific gravities, indices of refraction, and specific viscosities. The original paper was published in the *Memoirs, Imperial University, Kyoto,* 3, 3, p. 63, (1911), and a brief abstract of it in the

The method described in this communication is based on the obvious principle that two measurements are necessary and sufficient to determine the composition of a ternary mixture. Ordinary physical properties being chosen, the measurements are simple and the method is very rapid, after the two physical properties have been fully enough ascertained for mixtures of a given set of three substances. The tables below reproduce a complete set of such preliminary measurements for mixtures of toluene, carbon tetrachloride, and ethylene bromide. These data were needed in this laboratory in connection with a quantitative study of fractional distillation. They will, I believe, prove valuable in other physico-chemical studies as well, particularly in connection with the theory of liquid mixtures, and are, therefore, reproduced in full. It will be seen that instead of determining only two physical properties, which would have been sufficient for purely analytical purposes, I determined three, *viz.*, the specific volumes, the boiling points, and the indices of refraction. Experience has taught that even in analytical work a knowledge of the third property is not useless.

Ternary mixtures are now generally represented by means of an equilateral triangle, and in part of my work this was the mode of representation employed. However, different modes of graphic representation were employed in the more essential parts of the work.

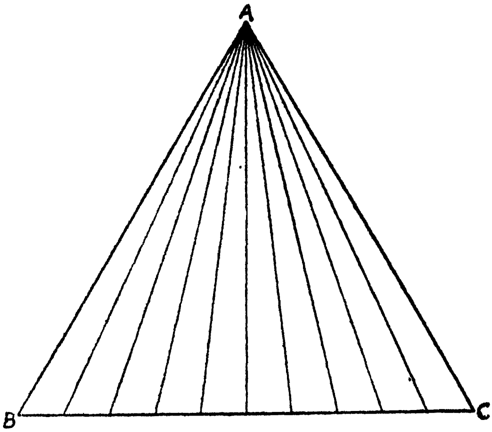

Fig. 1.

If, in an equilateral triangle (Fig. 1) each of whose sides represents 100 units, a straight line be drawn from a vertex, A, to any point on the side opposite, then all points on the line will represent mixtures containing two of the components, B and C, in a fixed ratio. Such mixtures may be consid-

Chemisches Zentralblatt, 2, 7, p. 437 (1911). The method employed by Horiba is, however, different in many respects from that described in the present communication and has yielded much less accurate results. This footnote is added in the proof.

[1] Schreinemakers, *Z. physik. Chem.*, 35, 459 (1900)

[2] Barrell, Thomas and Young, *Phil. Mag.*, [5] 37, 8 (1894)

ered as made up by mixing one of the three substances, A, with varying amounts of a binary mixture containing the other two substances B and C, in the fixed ratio just referred to. In other words, each line within the triangle in Fig. 1 may be thought of as representing all possible *binary* mixtures of the component A with a certain liquid which is itself a certain binary mixture of B and C.

If now some physical property, say the specific volumes, were determined for a set of mixtures along any such line within the triangle, then the graphic representation may be transferred to ordinary rectangular coördinates as follows: The origin of the abscissa may represent 0% and the farthest point to the right 100% of component A. At the same time these points will represent, respectively, 100 and 0% of the binary mixtures of B and C involved. The ordinates corresponding to the various abscissae may represent the physical property on a suitable scale. Then the same diagram may be used with reference to a second of the straight lines within the triangle. Now, the abscissa will represent the same percentages of A as before; only the new binary mixture will, of course, have a different composition than in the first case. The new ordinates will give a second curve on the diagram. In this manner a curve may be obtained corresponding to each of the straight lines within the triangle. Such sets of curves will be shown in Figs. 3, 4 and 5 further on. On such a diagram the two extreme curves may correspond to the two sides AB and AC of the equilateral triangle, and, therefore, represent binary mixtures in the true sense of the term. The data corresponding to each physical property measured will thus be represented by a separate set of curves.

Two sets of curves having been determined, the analysis of any ternary mixture of the components A, B, and C is very simple. The two physical properties are measured for the unknown mixture. Assuming that we deal with the boiling points and the specific volumes, it is evident that we may have an infinite number of mixtures that have the same boiling point as the unknown mixture, and likewise we may have an infinite number of mixtures that have the same specific volume as the unknown mixture. But usually only one mixture can have that boiling point and at the same time that specific volume. The composition of this mixture is determined as follows: At the level representing the boiling temperature of the unknown mixture a line is drawn across the curves parallel to the abscissa. This line will cut a certain number of curves. The percentage of A is read where the line cuts each curve, and, since the ratio of B to C is known for each curve, the percentages of these two components are readily calculated. Then on coördinate paper the per cents. of B are plotted as the ordinates, and the per cents. of A as the abscissae. In this manner, a curve is obtained representing all mixtures that have the same boiling point as the unknown mixture. This procedure is repeated for the specific volume, and thus a second curve is obtained representing all mixtures having the same specific volume as the unknown mixture. The two curves will intersect as shown, for example, in Fig. 2. *At the point of intersection the per cents. of A and B are read off, and the per cent. of C is obtained by difference. And this is the composition of the unknown mixture.* It is obvious that the accuracy of the method is greatest when physical properties are chosen that differ most widely for the three components.

In order to increase the reliability of the method, I decided to determine, as already stated, not two, but three physical properties, namely, the boiling points, the specific volumes, and the refractive indices. In connection with the latter, however, it was found more convenient to plot the *angles* as directly observed on a Pulfrich refractometer.

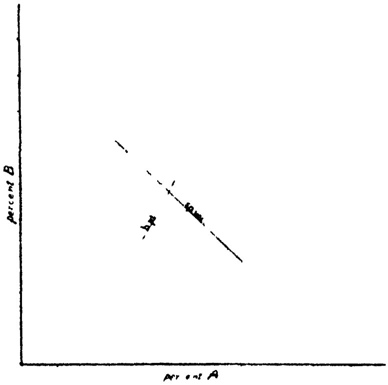

Fig. 2.

The liquids chosen for the experiments were toluene, carbon tetrachloride, and ethylene bromide. These liquids exhibit sufficiently wide differences in the three physical properties to permit of accurate analysis, as is evident from the following table:

TABLE I.

Substance	$C_6H_5CH_3$.	CCl_4.	$C_2H_4Br_2$.
Refractive angle at 25°	39.366°	45 367°	31.350°
Specific volume at 25°	1.1594	0.6297	0 4593
Boiling point under 749.0 mm.	110.11°	76.87°	130.23°

Great care was observed in the purification of the substances. The carbon tetrachloride and the toluene were Kahlbaum's. They were dried over calcium chloride and distilled with the aid of a five-bulb LeBel-Henninger column. Only the large middle fractions that passed over within 0.1° were taken. The ethylene bromide was made in this laboratory. After drying for several days over calcium chloride, it was distilled three times with the LeBel-Henninger column. Since ethylene bromide absorbs moisture very rapidly from the atmosphere, care was taken that the distillate did not come into contact with the air. Only the large middle fraction that passed over within 0.2° was taken.

The boiling points of the mixtures were determined in an Oddo ebullioscope, which was connected with a 100-liter manostat tank. The manostat was connected, in turn, with a source of compressed air, with suction, and with a large mercury manometer. This permitted the various boiling points to be observed under the same pressure. The pressure employed in these determinations was 749 mm. (corrected to 0°), which happens to be the average atmospheric pressure at Worcester.

The refractive angles of the mixtures were found by means of an excellent Pulfrich refractometer (new construction). The cup of the refractometer was kept at 25° by a stream of water from the same thermostat in which the mixtures to be analyzed were kept. The washer on the cap consisted of rubber which was painted over with collodion. The collodion was denitrated by treating the washer with ammonium sulphide. This made the washer elastic, and permitted the closing of the cup so that no measurable loss by evaporation could occur. The mixtures were allowed to remain in the cup for five minutes before the final reading was taken. In order to transform the angles given in my tables into the indices, the usual formula should be employed: $n = \sqrt{N^2 - \sin^2 e}$, where n denotes the index of refraction, N = 1.62197, and e is the angle observed.

The specific volumes of the mixtures were determined in 50 cc. specific gravity bottles at 25°.

The following procedure was used in making up the desired mixtures: The binary mixtures corresponding to those of the base of the triangle in Fig. 1 were made up of toluene and ethylene bromide, since these were the less volatile components. These binary mixtures will be referred to below as "fundamental mixtures." Carbon tetrachloride was considered as the third component, and altogether 111 samples were examined, including the three pure substances and an evenly graded set of binary and ternary mixtures. The measurements are reproduced in Tables II to XII, inclusively, the composition of each fundamental binary mixture which was mixed with increasing proportions of carbon tetrachloride being given at the head of each table.

In plotting the sets of curves for the boiling points, refractive angles, and specific volumes with the percentage of carbon tetrachloride as the abscissa in each case, the first two cases were found to give rather disappointing results; the curves, namely, ran closely together and finally

TABLE II.—FIRST FUNDAMENTAL MIXTURE: 100% $C_6H_5CH_3$, 0% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	110.11°	39.366°	1.1594
9.66	107.09	39.650	1.1079
20.00	103.87	40 017	1.0528
31.21	100.68	40.383	0.9996
39.88	97.85	40.733	0.9552
49.88	94.26	41.300	0.8952
60.29	90.72	41.833	0.8391
69.94	87.48	42.517	0.7882
80.04	84.00	43.300	0.7344
89.89	80.52	44.250	0.6821
100.0	76.87	45.367	0.6297

TABLE III.—SECOND FUNDAMENTAL MIXTURE: 90% $C_6H_5CH_3$, 10% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	110.80°	39.117°	1.0876
9.64	107.44	39.450	1.0412
19.79	104.07	39.817	0.9965
29.93	100.75	40.233	0.9501
39.97	97.21	40.717	0.9034
49.97	93.92	41.233	0.8596
59.99	90.49	41.850	0.8124
69.91	87.12	42.533	0.7662
79.93	83.71	43.333	0.7203
90.14	80.19	44.283	0.6739

TABLE IV.—THIRD FUNDAMENTAL MIXTURE: 80% $C_6H_5CH_3$, 20% $C_2H_4Br_2$.

% CCl_4	Boiling point.	Refractive angle.	Specific volume.
0	111.61°	38.833°	1.0184
10.65	107.69	39.250	0.9770
20.09	104.17	39.650	0.9401
29.84	100.72	40.083	0.9021
40.27	96.90	40.617	0.8615
50.41	93.49	41.183	0.8223
60.42	90.03	41.817	0.7836
70.24	86.71	42.550	0.7451
79.93	83.49	43.333	0.7076
90.06	80.08	44.300	0.6674

TABLE V.—FOURTH FUNDAMENTAL MIXTURE: 70% $C_6H_5CH_3$, 30% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	112.63°	38.502°	0.9507
10.05	108.44	38.967	0.9180
20.05	104.50	39.400	0.8863
30.57	100.41	39.933	0.8626
39.93	96.69	40.450	0.8220
50.37	93.18	41.100	0.7884
59.84	89.84	41.733	0.7583
69.90	86.60	42.467	0.7264
79.99	83.21	43.350	0.6930
89.51	79.99	44.333	0.6602

TABLE VI.—FIFTH FUNDAMENTAL MIXTURE: 60% $C_6H_5CH_3$, 40% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	113.80°	38.083°	0.8785
9.70	109.37	38.583	0.8543
19.91	104.79	39.117	0.8289
29.89	100.64	39.667	0.8040
40.06	96.52	40.333	0.7781
49.95	93.00	40.967	0.7537
59.99	89.47	41.683	0.7293
70.03	86.14	42.467	0.7035
79.90	82.99	43.333	0.6790
89.60	79.79	44.350	0.6533

TABLE VII.—SIXTH FUNDAMENTAL MIXTURE: 50% $C_6H_5CH_3$, 50% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	115.05°	37.600°	0.8113
9.87	109.87	38.167	0.7935
20.34	104.60	38.817	0.7744
29.82	100.63	39.383	0.7573
39.87	96.33	40.100	0.7386
50.06	92.51	40.850	0.7199
59.90	88.68	41.650	0.7026
69.93	85.62	42.417	0.6865
79.95	82.61	43.350	0.6658
90.15	79.70	44.350	0.6472

TABLE VIII.—SEVENTH FUNDAMENTAL MIXTURE: 40% $C_6H_5CH_3$, 60% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	116.68°	36.933°	0.7390
9.80	110.71	37.633	0.7283
19.91	105.12	38.350	0.7170
29.85	100.27	39.083	0.7061
40.06	95.91	39.867	0.6952
49.94	92.46	40.683	0.6840
59.87	88.68	41.517	0.6734
69.93	85.37	42.400	0.6625
79.91	82.42	43.333	0.6515
90.06	79.48	44.367	0.6398

TABLE IX.—EIGHTH FUNDAMENTAL MIXTURE: 30% $C_6H_5CH_3$, 70% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	118.54°	36.133°	0.6699
10.11	111.39	36.967	0.6660
19.76	105.32	37.833	0.6618
29.71	100.01	38.700	0.6577
39.99	95.42	39.600	0.6537
50.05	92.00	40.617	0.6494
60.16	88.03	41.450	0.6455
69.95	84.99	42.367	0.6414
79.88	82.12	43.350	0.6373
89.52	79.49	44.350	0.6333

TABLE X.—NINTH FUNDAMENTAL MIXTURE: 20% $C_6H_5CH_3$, 80% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	121.04°	35.033°	0.6002
9.88	112.51	36.083	0.6032
20.03	105.33	37.167	0.6059
30.47	99.55	38.217	0.6088
40.14	94.79	39.250	0.6118
49.93	90.95	40.267	0.6146
59.85	87.69	41.317	0.6177
69.92	84.51	42.333	0.6207
80.11	81.61	43.383	0.6236
89.83	79.33	44.367	0.6264

TABLE XI.—TENTH FUNDAMENTAL MIXTURE: 10% $C_6H_5CH_3$, 90% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	124.33°	33.550°	0.5310
10.21	113.49	34.917	0.5408
20.21	105.04	36.300	0.5508
29.96	98.98	37.583	0.5604
39.91	94.31	38.783	0.5701
50.02	90.23	40.017	0.5801
60.15	87.05	41.167	0.5911
69.99	84.21	42.267	0.6000
80.17	81.49	43.367	0.6102
89.95	79.17	44.367	0.6193

TABLE XII.—ELEVENTH FUNDAMENTAL MIXTURE: 0% $C_6H_5CH_3$, 100% $C_2H_4Br_2$.

% CCl_4.	Boiling point.	Refractive angle.	Specific volume.
0	130.23°	31.350°	0.4593
10.62	114.96	33.333	0.4765
20.27	104.97	34.183	0.4940
29.86	98.34	36.750	0.5101
39.85	93.25	38.300	0.5274
49.90	89.50	39.717	0.5445
60.02	86.35	41.033	0.5616
70.64	83.70	42.200	0.5787
80.02	81.04	43.367	0.5964
90.13	78.90	44.383	0.6187

crossed. It was suggested that the curves might appear better distributed if ethylene bromide were considered as the third component, and were, therefore, plotted as the abscissa. I therefore undertook to recalculate all the values so that each curve should correspond to a certain ratio of toluene to carbon tetrachloride. The calculation was carried out in the following manner: Let x = per cent. carbon tetrachloride, y = per cent. ethylene bromide, and z = per cent. toluene. In the present sets of curves we have $z/y = \%C_6H_5CH_3/\%C_2H_4Br_2$. Let this ratio be denoted by A. What is needed is the ratio $z/x = \%C_6H_5CH_3/\%CCl_4$. Let this ratio be denoted by B. Then $y = B/Ax$ and $z = Bx$. But $x + y + z = 100$. Therefore, $x = 100/(1 + B/A + B)$, $z = Bx$ and $y = z/A$. Let, for example, the problem be to calculate a set of data for the boiling-point curve of mixtures containing toluene and carbon tetrachloride in the ratio $B = 9 : 1$. We substitute, in the equation just given, this value for B, while for the ratio A we use consecutively the values $9 : 1$, $8 : 2$, $7 : 3$, $6 : 4$, $5 : 5$, $4 : 6$, $3 : 7$, $2 : 8$, and $1 : 9$, corresponding to the ratios of the curves that have been found experimentally. This will lead to a series of values for x and y. Now at the value of x found for a certain ratio A, say $9 : 1$, we read off the boiling point on the curve corresponding to this ratio. Evidently this boiling point must also correspond to the value y found for the same ratio. Hence we plot the boiling point as ordinate and y

as the abscissa. Thus, the boiling points for the whole series of x's are read and re-plotted against the corresponding y's. This will give us the curve where $B = z/x = \%C_6H_5CH_3/\%CCl_4 = 90/10$. By thus assigning to B consecutively the values 8 : 2, 7 : 3, etc., we obtain the boiling points

TABLE XIII.—VALUES FOR THE BOILING-POINT CURVES.

Percentages of $C_2H_4Br_2$ ("third component").

$\%C_7H_8$ / $\%CCl_4$	0%. °C.	10%. °C.	20%. °C.	30% °C.	40%. °C.	50%. °C.	60%. °C.	70% °C.	80%. °C.	90%. °C.	100%. °C.
100/0	110.11	110.81	111.62	112.65	113.77	115.05	116.69	118.56	121.00	124.43	130.23
90/10	106.98	107.80	108.79	109.95	111.28	112.78	114.60	116.85	119.83	123.81	.
80/20	103.87	104.77	105.88	107.25	108.63	110.28	112.39	114.98	118.51	123.15	.
70/30	100.74	101.70	102.84	104.25	105.99	107.80	110.11	113.02	116.97	122.40	
60/40	97.50	98.58	99.85	101.45	103.18	105.20	107.79	111.06	115.54	121.57	..
50/50	94.21	95.39	96.77	98.47	100.26	102.44	105.28	108.96	113.69	120.59	.
40/60	90.82	92.18	93.70	95.50	97.57	99.87	102.70	106.68	112.02	119.57	..
30/70	87.48	88.98	90.65	92.53	94.71	97.32	100.48	104.61	110.30	118.62	..
20/80	84.00	85.65	87.50	89.51	91.85	94.67	98.10	102.46	108.60	117.50	..
10/90	80.50	82.26	84.33	86.58	89.05	92.01	95.63	100.40	107.03	116.34	.
0/100	76.87	78.81	81.06	83.61	86.35	89.46	93.18	98.10	105.21	115.00	-

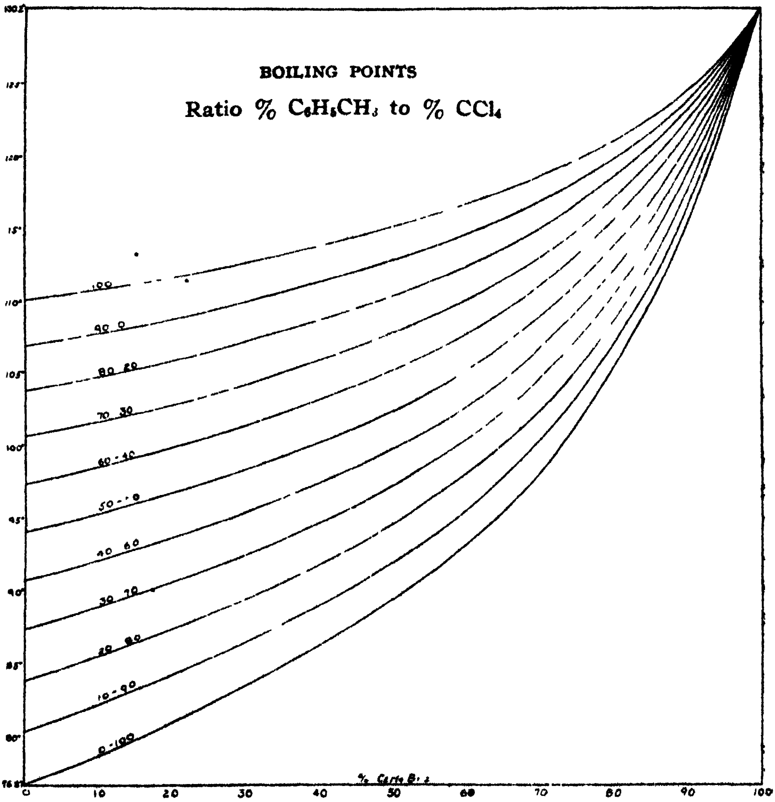

Fig. 3.

TABLE XIV.—VALUES FOR THE SPECIFIC VOLUMES

Percentages of $C_2H_4Br_2$ ("third component").

$\frac{\% C_7C_8}{\% CCl_4}$.	0%.	10%.	20%.	30%.	40%.	50%.	60%.	70%	80%.	90%	100%.
100/0	1.1593	1.0890	1.0190	0.9489	0.8790	0.8092	0.7395	0.6701	0.6002	0.5305	0.4596
90/10	1.1043	1.0405	0.9765	0.9124	0.8484	0.7844	0.7194	0.6545	0.5896	0.5244	
80/20	1.0530	0.9940	0.9348	0.8755	0.8164	0.7572	0.6979	0.6381	0.5788	0.5190	
70/30	1.0000	0.9463	0.8922	0.8382	0.7847	0.7309	0.6770	0.6222	0.5680	0.5139	
60/40	0.9463	0.8977	0.8496	0.8012	0.7529	0.7043	0.6558	0.6065	0.5575	0.5086	
50/50	0.8932	0.8502	0.8067	0.7638	0.7205	0.6772	0.6337	0.5903	0.5470	0.5031	
40/60	0.8420	0.8035	0.7654	0.7278	0.6893	0.6510	0.6125	0.5740	0.5360	0.4980	
30/70	0.7873	0.7550	0.7222	0.6897	0.6572	0.6246	0.5918	0.5585	0.5257	0.4923	
20/80	0.7349	0.7072	0.6800	0.6527	0.6249	0.5971	0.5696	0.5421	0.5146	0.4870	
10/90	0.6820	0.6599	0.6378	0.6155	0.5933	0.5711	0.5489	0.5262	0.5040	0.4816	.
0/100	0.6300	0.6130	0.5958	0.5789	0.5620	0.5450	0.5280	0.5109	0.4939	0.4768	0.4596

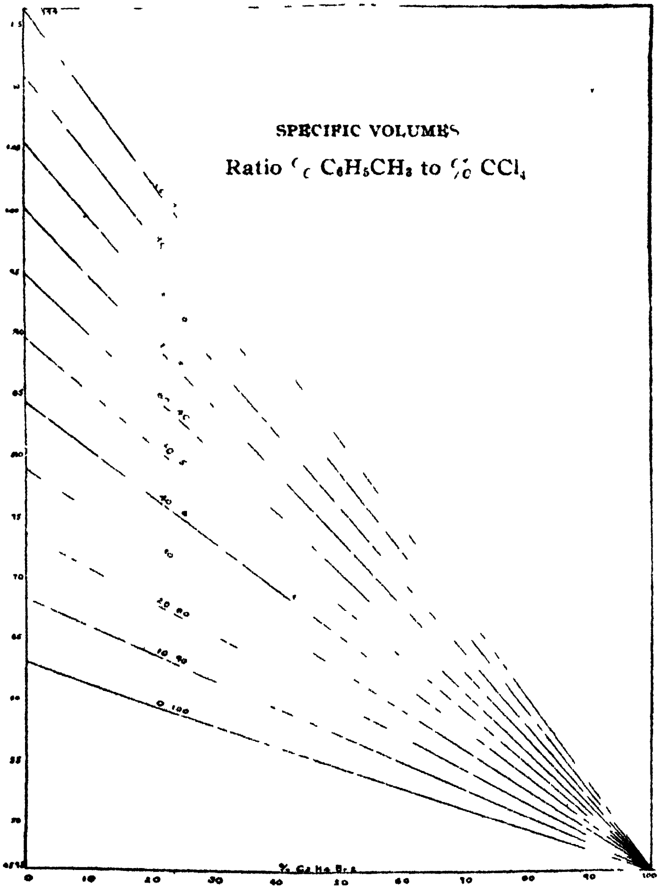

Fig. 4.

TABLE XV.—VALUES FOR THE REFRACTIVE ANGLES.

Percentages of toluene ("third component").

$\frac{\% \; CCl_4}{\% \; C_2H_4Br_2}$	0%.	10%.	20%.	30%.	40%.	50%.	60%.	70%.	80%.	90%.	100%.
100/0	45.37°	44.26°	43.30°	42.52°	41.86°	41.28°	40.78°	40.34°	39.98°	39.66°	39.37°
90/10	44.39	43.42	42.63	42.00	41.46	40.96	40.54	40.17	39.87	39.60	..
80/20	43.33	42.58	41.98	41.45	41.02	40.62	40.30	40.01	39.77	39.56	.
70/30	42.20	41.68	41.25	40.88	40.56	40.28	40.04	39.83	39.67	39.51	.
60/40	41.01	40.74	40.50	40.28	40.10	39.93	39.80	39.67	39.56	39.46	..
50/50	39.73	39.70	39.67	39.64	39.61	39.57	39.53	39.49	39.44	39.40	.
40/60	38.32	38.62	38.85	39.01	39.10	39.19	39.26	39.30	39.32	39.34	..
30/70	36.80	37.47	37.97	38.35	38.60	38.81	38.98	39.10	39.20	39.28	..
20/80	35.13	36.20	37.05	37.65	38.08	38.42	38.69	38.90	39.07	39.23	..
10/90	33.22	34.89	36.06	36.89	37.53	38.02	38.39	38.70	38.95	39.17	..
0/100	31.25	33.51	35.03	36.13	36.94	37.60	38.08	38.49	38.83	39.11	..

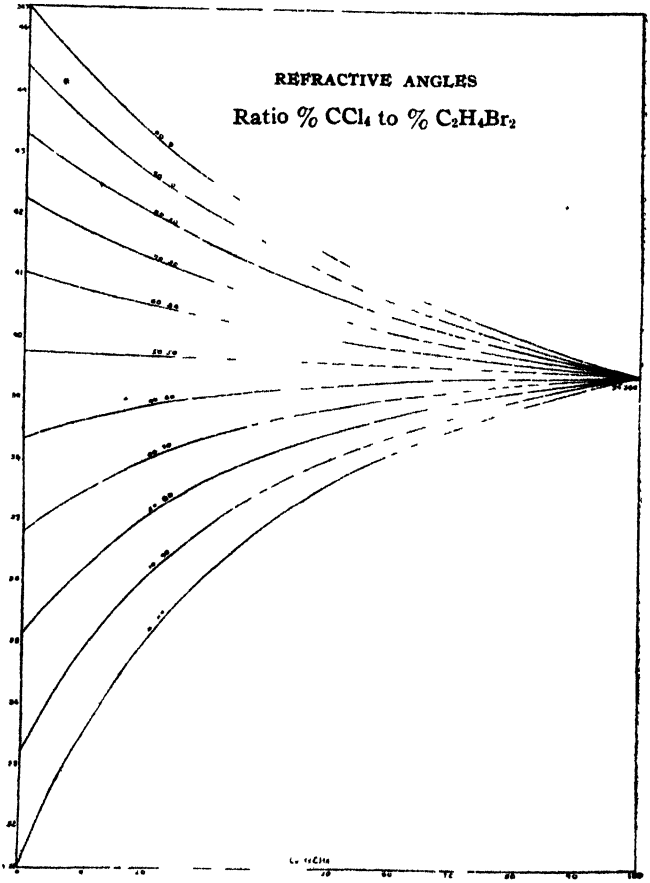

Fig. 5.

required for all the other curves in the new set, where ethylene bromide is regarded as the third component, that is, as the substance mixed with various binary mixtures of toluene and carbon tetrachloride. These boiling points are reproduced in Table XIII and graphically in Fig. 3.

Similarly recalculated values of the specific volumes are reproduced in Table XIV and Fig. 4. In the case of the refractive angles it was found necessary to recalculate the original results, using toluene as the "third component." The angles so obtained are reproduced in Table XV and Fig. 5.

In order to facilitate the reproduction of the curves, the values, calculated as just explained, were carefully plotted on a large scale, and the curves smoothed. The data tabulated below are those read off from the smoothed curves. In the tables, the percentage of the "third component" is given by the first horizontal line, while the first vertical column of figures gives the ratios of the "fundamental mixtures" corresponding to the several curves.

In order to test the availability of these data for analytical purposes, eight mixtures were prepared by carefully weighing the components, and then analyzed by the method outlined above. It was found that the curves representing respectively, mixtures of the same boiling point, the same specific volume, and the same refractive angle do not all intersect

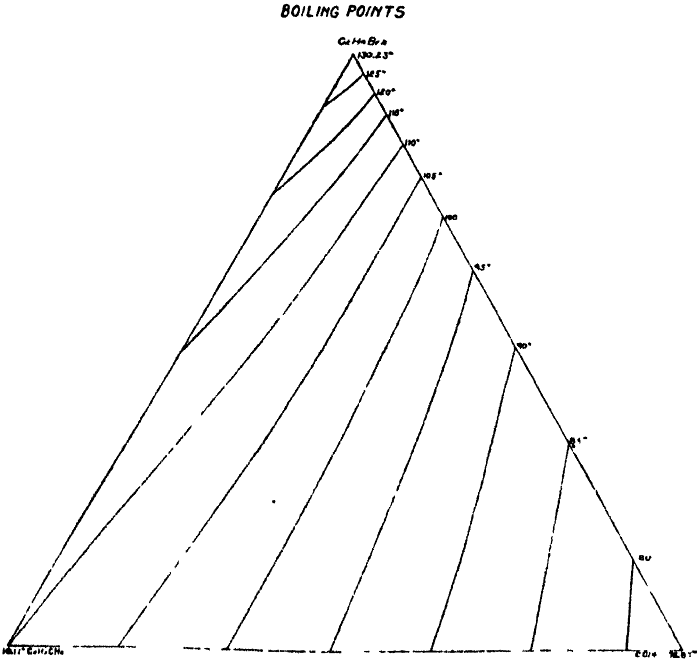

Fig. 6.

in exactly one point, as they should. This is obviously due to slight errors in the predetermined curves, or else to errors in observing the physical properties of the mixtures analyzed. However, the three points of intersection lie very close to one another. The point representing the true composition invariably falls on the specific-volume curve. This indicates that the pre-determined specific-volume curves are the most accurate, as might be expected. Consequently, the values for the mixtures were read in each case at the intersection of the specific-volume curve with the boiling-point curve on the one hand, and with the refractive-angle curve on the other hand. The mean if these two values was taken as the composition of the mixture.

The results of the eight consecutive analyses are reproduced below. In each case I give the boiling point, the refractive angle, and the specific volume as found for the mixture. The column under V + R represents the percentage of the components as shown by the intersection of the specific-volume curve with the refractive-angle curve, while the column under V + T represents the values for the intersection of the specific-volume curve with the boiling-temperature curve.

Table XVI.—Mixture 1

Boiling point under 749 mm. . . .	80.55°
Refractive angle at 25°.	43.84°
Specific volume at 25°. . . .	0.6325

	V + R.	V + T.	Found. Mean.	True composition.	Diff %
% CCl_4.	85.20	84.80	85.00	84.93	+0.07
% $C_2H_4Br_2$	10.80	11.05	10.92	10.93	—0.01
% C_7H_8.	4.00	4.15	4.08	4.14	—0.06

Table XVII.—Mixture 2

Boiling point under 749 mm.	86.73°
Refractive angle at 25°.	42.117°
Specific volume at 25°.	0.6800

	V + R.	V + T	Found. Mean.	True composition.	Diff. %
% CCl_4.	66.35	66.55	66.45	66.38	+0.07
% $C_2H_4Br_2$.	18.25	18.15	18.20	18.13	+0.07
% C_7H_8	15.40	15.30	15.35	15.49	—0.14

Table XVIII.—Mixture 3.

Boiling point at 749 mm.	97.38°
Refractive angle at 25°.	39.93°
Specific volume at 25°.	0.7593

	V + R.	V + T.	Found. Mean.	True composition.	Diff. %
% CCl_4.	36.45	37.50	36.98	37.04	—0.06
% $C_2H_4Br_2$.	29.55	28.75	29.15	29.14	+0.01
% C_7H_8.	34.00	33.75	33.87	33.82	+0.05

TABLE XIX.—MIXTURE 4.

Boiling point at 749 mm	103.5°
Refractive angle at 25°	37.77°
Specific volume at 25°	0.6356

	V + R.	V + T.	Found. Mean.	True composition	Diff. %
% CCl_4	22.50	23.00	22.75	22.88	−0.13
% $C_2H_4Br_2$	57.80	57.50	57.65	57.54	+0.11
% C_7H_8	19.70	19.50	19.60	19.58	+0.02

TABLE XX.—MIXTURE 5.

Boiling point at 749 mm	109.85°
Refractive angle at 25°	39.330
Specific volume at 25°	0.8941

	V + R.	V + T	Found. Mean	True composition	Diff. %.
% CCl_4	2.20	1.65	1.925	1.89	+0.035
% $C_2H_4Br_2$	4.20	4.55	4.375	4.47	−0.095
% C_7H_8	93.60	93.80	93.700	93.64	+0.060

TABLE XXI.—MIXTURE 6.

Boiling point at 749 mm	111.21°
Refractive angle at 25°	35.125°
Specific volume at 25°	0.5374

	V + R.	V + T.	Found. Mean.	True composition.	Diff. %.
% CCl_4	8.15	8.10	8.12	8.13	+0.01
% $C_2H_4Br_2$	79.55	79.10	79.33	79.59	+0.26
% C_7H_8	12.30	12.80	12.55	12.28	−0.27

TABLE XXII.—MIXTURE 7

Boiling point at 749 mm	112.5°
Refractive angle at 25°	34.64°
Specific volume at 25°	0.5202

	V + R.	V + T.	Found. Mean.	True composition.	Diff. %.
% CCl_4	11.60	11.75	11.675	11.15	+0.52
% $C_2H_4Br_2$	82.60	82.50	82.55	82.90	−0.35
% C_7H_8	5.80	5.75	5.775	5.95	−0.17

TABLE XXIII.—MIXTURE 8.

Boiling point at 749 mm.	122.23°
Refractive angle at 25°	33.10°
Specific volume at 25°	0.4980

	V + R.	V + T.	Found. Mean.	True composition.	Diff. %.
% CCl_4	4.10	3.90	4.00	3.49	−0.51
% $C_2H_4Br_2$	91.60	91.80	91.70	91.85	+0.15
% C_7H_8	4.30	4.30	4.30	4.66	+0.36

These results show that the method is quite accurate. The largest error occurs when the percentage of ethylene bromide is very great.

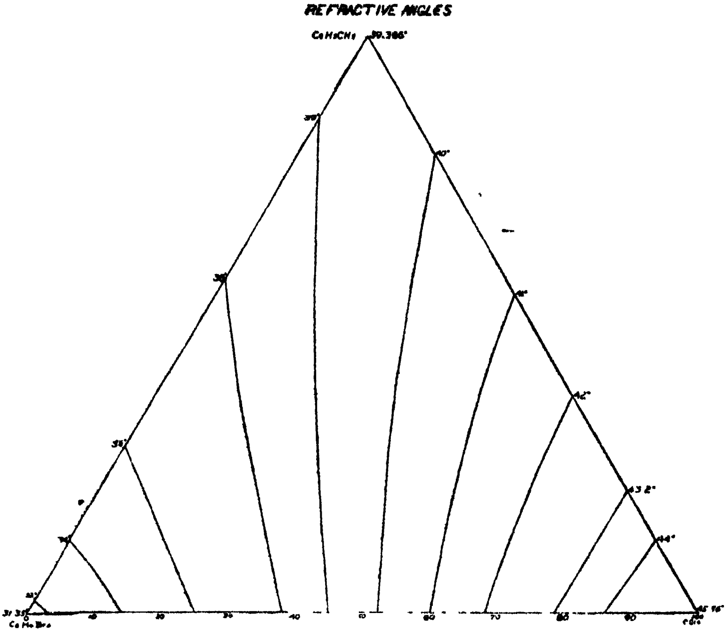
REFRACTIVE ANGLES
39°
40°
38°
41°
42°
35°
43.2°
44°
40
50
60
70
80
90

Fig. 7.

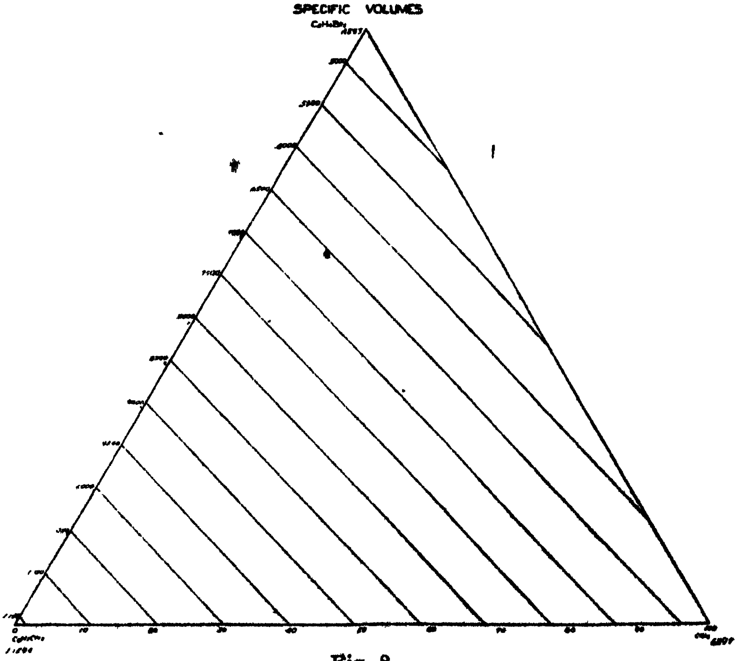
SPECIFIC VOLUMES
0
10
20
30
40
50
60
70
80
90

Fig. 8.

Evidently the curves are not very accurate in this region. The inaccuracy may be due to the fact that ethylene bromide takes up moisture from the atmosphere with extreme rapidity. This, of course, would affect the physical properties of the mixtures rich in this component to a considerable extent. But, as the analyses show, the errors even in that region do not exceed half a per cent. Since the completion of the work I have further used the method in a large number of cases, with similarly satisfactory results.

It seemed desirable to see how the curves would appear if drawn according to the Roozeboom method of representation, in equilateral triangles. Figs, 6, 7, and 8 represent, respectively, curves of equal boiling points, of equal refractive angles, and of equal specific volumes.

In conclusion, I wish to express my most sincere gratitude to Professor M. A. Rosanoff, at whose suggestion and under whose guidance this work was carried out. My thanks are also due to my friend, H. M. Potter, Assistant Professor of the Oklahoma Agricultural and Mechanical College, for a great deal of assistance in the experimental work.

WORCESTER, MASS

NOTE.

An Efficient Boiling Rod.--We have found the following forms of boiling rods very effective and having several advantages over the boiling capillaries and other means usually employed to prevent bumping. Crush a small piece of an alundum crucible or of a porous porcelain plate in a mortar to small particles about one-half millimeter in diameter. The material should not, however, be finely powdered. Place this coarse powder in a small porcelain crucible and heat it red hot over the blast lamp. Heat one end of a small glass rod 10-12 centimeters in length until it softens and dip it into the alundum particles, which will adhere to the rod. Heat the rod again and repeat two or three times until a suitable amount of alundum particles have gathered on the end of the rod. Finally heat the rod in the lamp until the particles adhere to the glass. Cool slowly and rub off any loose particles by rubbing the porous end through the fingers in a cloth or towel.

Another form of rod can be prepared by fusing one end of a narrow rectangular or trianglar piece of alundum or porous procelain into the end of a glass rod and bending the end of the rod in such a manner at the joint that the piece of alundum will lie on the bottom of the beaker or flask. The size of the plate can be varied and for some purposes larger plates may be used but for quantitative work it is best to have the piece as small as possible, because porcelain plates or alundum absorb acids and generally require repeated washings with hot water before they become neutral to the taste or to litmus. The boiling rod should be put in the solution when it reaches the boiling point, not before. GREGORY TOROSSIAN.

CLEVELAND, OHIO.

CORRECTION.

Page 228, line 4, should read "... $\gamma = 1.530\text{–}1.535$; .....".

Page 228, line 26–7, should read "...parallel to the α-γ plane".

GEORGE W. MOREY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY.
No. 230.]

THE PREPARATION AND PROPERTIES OF CERTAIN METHOXYLATED CARBINOLS, OLEFINS AND KETONES, DERIVED FROM TRIMETHYLGALLIC ACID.

BY MARSTON TAYLOR BOGERT AND ROBERT MELYNE ISHAM.

Received December 29, 1913.

1. Introductory.

In secondary and tertiary carbinols of types I and II, the introduction of methoxyl groups in place of one or more of the hydrogens of their

I. $C_6H_5.CH(OH)R.$ II. $C_6H_5.C(OH)R_2.$

phenyl nuclei causes interesting alterations in their properties.

As compared with triphenyl carbinol itself, von Baeyer and Villiger,[1] Kauffmann,[2] and others have shown that methoxylated triphenyl carbinols exhibit increased halochromism and increased basicity, and are more easily reduced to the corresponding methoxylated triphenyl methane.

Hell[3] attempted to prepare carbinols of type III by the action of the Barbier-Grignard reagent upon anisic aldehyde and upon *p*-methoxybenzophenone, but found that the expected carbinols were so unstable, that when the magnesium compounds were hydrolyzed with dilute acid, the corresponding olefins (IV) were obtained, and not the carbinols at all.

III. $CH_3O.C_6H_4.CR(OH)CH_2R_1$ ($R = H$ or C_6H_5).

IV. $CH_3O.C_6H_4.CR : CH.R_1$ ($R = H$ or C_6H_5).

The instability of these secondary and tertiary carbinols, he attributed to the influence of the para methoxyl group. He noted also that anisyl phenyl propene and other methoxylated olefins of similar structure, do not give dibromo addition products when treated with bromine, but yield preferably monobromo substitution products (V), apparently by

V. $CH_3O.C_6H_4.C(C_6H_5) : CBr.CH_3.$

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[1] *Ber.*, 35, 3013 (1902).

[2] *Ibid.*, 38, 2702 (1905); 41, 4423 (1908); 45, 766 (1912); 46, 3779, 3788 (1913).

[3] *Ibid.*, 37, 225, 457, 1429, 4188 (1904).

loss of HBr from an antecedent unstable dibromide. This instability of the dibromide cannot be referable, however, solely to the methoxyl group, since diphenyl propene shows an analogous behavior with bromine.

Having had occasion to carry out certain other syntheses with methyl trimethylgallate, a compound which is easily prepared in any desired amount, it was deemed worth while to study the carbinols and olefins obtainable therefrom, in the expectation that additional data bearing upon the influence of the methoxyl group would be secured, as the group is one of peculiar interest because of its frequent occurrence in natural products. Our results agree, in the main, with those obtained by previous workers in this field and, in addition, we have observed that the presence of the methoxyl groups in the phenyl nucleus of compounds of type VI materially heightens the reactivity of the halogen.

VI. $C_6H_5.C(R)(CH_2R)Cl$.

3,4,5-Trimethoxytriphenyl carbinol exhibits strong halochromism, and is very easily reduced to the trimethoxytriphenyl methane. It is more basic than triphenyl carbinol, but less basic than *p*-methoxytriphenyl carbinol. In other words, the *m*-methoxyl groups reduce the basicity of the *p*-methoxyl compound.

Experiments were carried out for the preparation of the following five carbinols of type VII by the Barbier-Grignard reaction, namely: (1)

VII. $(CH_3O)_3C_6H_2.C(OH)(CH_2R)_2$ (R = H or a radical).

trimethoxyphenyl dimethyl, (2) trimethoxyphenyl diethyl, (3) trimethoxyphenyl dipropyl, (4) trimethoxyphenyl diisoamyl, and (5) trimethoxyphenyl dibenzyl. When the magnesium compound was hydrolyzed with dilute acid, the following results were obtained: (1) gave chiefly olefin, although there was evidence of an unstable intermediate carbinol; (2) gave both carbinol and olefin, the former being very unstable; (3) and (4) gave olefin only and no carbinol; while (5) yielded a stable carbinol. The carbinol chlorides of (2) and (5) were quite unstable, readily losing HCl to give the olefin. By the action of dry hydrogen chloride upon an ether solution of either of these carbinols at 0°, the product was not the chloride, but the olefin. Klages[1] describes the chloride of phenyl diethyl carbinol as a colorless oil, which loses hydrochloric acid when heated alone or with pyridine, giving the corresponding olefin. Evidently the introduction of the methoxyl groups materially increases the instability of both the carbinol and the chloride. Klages[2] failed to obtain any reaction between phenyl dibenzyl carbinol and hydrogen chloride under conditions similar to those under which we obtained the chloride from the trimethoxyphenyl dibenzyl carbinol, so that the only conclusion to be drawn from the two cases is that the methoxyl groups appear to increase the mobility of the carbinol hydroxyl.

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[1] *Ber.*, 36, 3692 (1903).

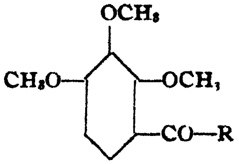
[2] *Ibid.*, 37, 1456 (1904).

In harmony with the observations of Hell, alluded to above, it was found that every one of the five olefins obtained by these reactions formed an unstable dibromo addition product, which lost hydrobromic acid with production of a monobromo substitution product.

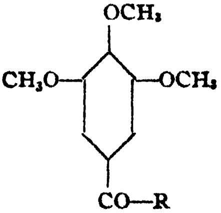
In an attempt to prepare the β-trimethoxyphenyl β-lactic acid by reduction of trimethylgalloyl acetic ester with activated aluminum, we obtained instead the corresponding trimethoxy cinnamic acid, showing that the intermediate secondary carbinol must have been unstable under the conditions of the experiment, losing a molecule of water to form the unsaturated acid, in the same way that the above tertiary carbinols lose water to form the olefins; and here, too, the methoxyl groups appear largely responsible for the instability of the carbinol.

Nencki,[1] Mannich and Hahn,[2] and others, have obtained ketones of type VIII by the application of the Friedel-Crafts reaction to trimethyl pyrogallol; but of the isomeric type IX, the only one we found in the literature at the time this work was undertaken was the 3,4,5-trimethoxy acetophenone prepared by Mauthner[3] from trimethylgallic aldehyde by the action of diazo methane, and from trimethylgalloyl acetic ester by hydrolysis with dilute sulfuric acid. We have succeeded in obtaining Mauthner's compound, and a number of others of this type (IX), by taking the olefins secured in our Grignard reactions and treating them with ozone, according to the Harries method:

VIII.



IX.



$$(CH_3O)_3C_6H_2.CR_1 : CHR + O_3 + H_2O = (CH_3O)_3C_6H_2.CR_1O + OCH.R + H_2O_2$$

The action of the ozone on the olefins with the longer chains was quite slow, in some cases 20 hours' treatment being insufficient to complete the reaction.

From the trimethoxy acetophenone, the corresponding chalkone (X) was prepared by condensation with benzaldehyde; and from the trimethylgalloyl acetic ester and resorcinol, the trimethoxyphenyl umbelliferone (XI).

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[1] *Ber.*, 27, 2738 (1894).

[2] *Ibid.*, 44, 1542 (1911).

[3] *J. prakt. Chem.*, [2] 82, 275 (1910).

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further established by the preparation of its met
to 3,5-dimethoxyquinone.

2. Experimental.

Trimethylgallic acid, $(3,4,5)(CH_3O)_3C_6H_2.COOH$, was pre
methylation of gallic acid with dimethyl sulfate and sodium
in aqueous solution, essentially as described by Graebe and Martz, and by Perkin and Weizmann,[6] purifying the crude acid by recrystallization from very dilute acetic acid, in presence of boneblack. As thus prepared, it formed colorless needles, melting at 168°,[7] in agreement with the results recorded by other investigators. Yield of pure acid, 65%.

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[1] *Gazz. chim. ital.*, 18, 215 (1888).

[2] *Ber.*, 30, 2330 (1897).

[3] Hertzig and Pollack, *Monatsh.*, 23, 700 (1902); Graebe and Martz, *Ber.*, 36, 215 (1903).

[4] *Ber.*, *Loc. cit.*; *Ann.*, 340, 221 (1905).

[5] *Ann.*, 340, 219 (1905).

[6] *J. Chem. Soc.*, 89, 1655 (1906).

[7] The melting points recorded in this paper were all taken with Anschütz standard short-scale thermometers unless otherwise stated.

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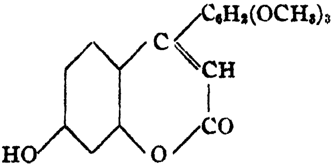

—Two grams of ethyl trimethylgalloyl acetate and 0.77 gram resorcinol were dissolved in 15 cc. 73% sulfuric acid at 0°.[4] The solution rapidly turned a deep orange, and on standing over night deposited a mass of yellowish crystals. Ice was added in considerable quantity, the mixture left at 0° for an hour, the crystals were filtered out, washed with water, and recrystallized from alcohol. The umbelliferone was thus obtained as a

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[1] *J. Chem. Soc.*, 95, 254 (1909).

[2] *Loc. cit.*

[3] Perkin and Weizmann, *loc. cit.*

[4] Compare Von Pechmann and Duisberg, *Ber.*, 16, 2126 (1883); Von Pechmann and Hanke, *Ibid.*, 34, 356 (1901); Von Kostanecki and Weber, *Ibid.*, 26, 2907 (1893).

colorless micro-crystalline solid, sintering at about 245°, and melting with decomposition at about 253°.

0.2144 g. substance: 0.5162 g. CO_2, 0.0959 g. H_2O. Calcd. for $C_{18}H_{16}O_6$: C, 65.83%; H, 4.94%. Found: C, 65.53%; H, 5.00%.

3,4,5-Trimethoxycinnamic Acid (Methyl Sinapinic Acid), $(CH_3O)_3C_6H_2$.CH : CH.COOH.—Ten grams trimethylgalloyl acetic ester were dissolved in 150 cc. 95% alcohol and 7 grams activated aluminum[1] added. A lively reaction ensued, with production of hydrogen, which was at first largely absorbed. After standing for two days, the mixture was filtered and the insoluble aluminum alcoholate washed with alcohol Upon concentration of the alcoholic filtrate, a colorless oil of geranium-like odor remained which could not be brought to crystallization. It was therefore dissolved in dilute alcohol and saponified by warming for four hours with dilute sodium hydroxide solution. The alkaline solution was acidified with dilute hydrochloric acid, evaporated to dryness at 100°, the residue extracted with absolute alcohol, the alcoholic extract concentrated to crystals, and the crystals recrystallized from benzene. Colorless needles were obtained, melting at 126.8°. Yield, 5 grams.

0.2176 g. substance: 0.4796 g. CO_2, 0.1160 g. H_2O. Calcd. for $C_{12}H_{14}O_5$: C, 60.50%; H, 5.88%. Found: C, 60.11%; H, 5.93%

Gadamer[2] obtained this acid by direct methylation of sinapinic acid, and called it, therefore, methylsinapinic acid. It was later prepared by Mauthner[3] from the trimethoxybenzaldehyde by the Perkin reaction. Although our product melts about 3° higher, it was found to be identical with the product of Gadamer and Mauthner. A solution of the acid in chloroform rapidly decolorized a similar solution of bromine.

Syringic Acid, $(3,5)(CH_3O)_2C_6H_2(OH)(4)COOH(1)$.—Thirty grams trimethylgallic acid were added slowly, with constant stirring, to 150 grams 20% fuming sulfuric acid, the temperature being kept below 40°. The gallic acid dissolved with production of a deep red solution and with evolution of heat, and at the same time the characteristic aromatic odor of syringic acid became apparent. The solution was kept at 40° for 30 minutes, and on cooling it set to a crystalline mass. An equal volume of water was added, the mixture let stand for eight hours, and the crystals were then filtered out, washed with cold water and dried. Yield, 25 grams. Recrystallized from water, it was obtained in colorless needles, melting at 204°. Graebe and Martz[4] give the melting point as 204° (corr.).

0.2010 g. substance: 0.4024 g. CO_2, 0.0949 g. H_2O. Calcd. for $C_9H_{10}O_5$: C, 54.54%; H, 5.05%. Found: C, 54.59%; H, 5.22%.

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[1] Compare Wislicenus, *J. prakt. Chem.*, [2] **54**, 54 (1896).

[2] *Arch. Pharm.*, **235**, 109 (1897); *Ber.*, **30**, 2331 (1897).

[3] *Ibid.*, **41**, 2531 (1908).

[4] *Ann.*, **340**, 220 (1905).

Ten grams of the acid were suspended in 70 cc. methyl alcohol and dry hydrogen chloride passed in until all was dissolved and the solution thoroughly saturated with the hydrogen chloride. It was then allowed to to stand for 30 minutes, evaporated to dryness, and the residue freed from hydrogen chloride by repeated evaporation with methyl alcohol. The residual brownish crystalline mass, recrystallized from water, gave beautiful colorless needles of the hydrated ester, melting at 83–4°. Dehydrated at 110°, the anhydrous ester melted at 106–7°. Yield of anhydrous ester, 8 grams. These melting points agree with the observations of Graebe and Martz.[1]

Two grams of syringic acid and two and a half of sodium chromate were dissolved in 100 cc. of water by warming, and dilute sulfuric acid was added slowly to slight excess. An immediate evolution of carbon dioxide resulted. When cold, the solution was extracted with chloroform, the chloroform evaporated, and the residue recrystallized from acetic acid. The characteristic yellow needles of 3,5-dimethoxyquinone were obtained, melting sharply at 255°, this melting point being unaltered when the substance was mixed with an equal amount of 3,5-dimethoxyquinone prepared in a different synthesis.

3,4,5-Trimethoxytriphenyl Carbinol, $(CH_3O)_3C_6H_2.C(C_6H_5)_2.OH$.- 5.2 grams magnesium turnings were placed in a flask connected by means of a brominating tube with a return condenser. Dry ether was added to cover these turnings, then 40 grams of brombenzene, and finally a small crystal of iodine. In a few minutes, a vigorous reaction began, which was moderated from time to time by external cooling, and was completed by warming for an hour at 100°. After cooling, a suspension of 18 grams of finely powdered methyl trimethylgallate in 100 cc. of dry ether was run in slowly. The mixture was let stand for several hours to complete the reaction, after which the magnesium compound was decomposed by the addition of ice and dilute sulfuric acid, the carbinol separating at once as a white, granular solid. Washed with ether and recrystallized from alcohol, it was obtained in colorless elongated hexagonal crystals, melting sharply at 189°; insoluble in water, nearly insoluble in ether, slightly soluble in ligroin, rather easily soluble in methyl or ethyl alcohol, acetic acid, chloroform or benzene. Yield of carbinol, 25 to 27 grams.

0.1971 g. substance: 0 5452 g. CO_2, 0 1113 g. H_2O. Calcd. for $C_{22}H_{22}O_4$: C, 75.42%; H, 6.28%. Found: C, 75.39%; H, 6.29%.

This carbinol exhibits marked halochromism, dissolving in concentrated sulfuric acid with production of a deep red solution. Examined by the method of von Baeyer and Villiger,[2] its basicity lies considerably below that of *p*-methoxytriphenyl carbinol. While triphenyl carbinol itself

[1] *Loc. cit.*

[2] *Ber.*, 35, 3021 (1902).

requires 4.3 cc. of alcohol, per millimole, to discharge the color of the sulfuric-acetic solution, and *p*-methoxytriphenyl carbinol requires 26.9 cc., the 3,4,5-trimethoxytriphenyl carbinol requires only 15.4 cc. From these figures, the relative basicity of the three carbinols would appear to be *p*-methoxytriphenyl : trimethoxytriphenyl : triphenyl = 6.3 : 3.6 . 1. The presence of the *m*-methoxyl groups therefore seems to reduce the basicity of the *p*-methoxyl group in such carbinols.

3,4,5-Trimethoxytriphenyl Methyl Chloride, $(CH_3O)_3C_6H_2.C(C_6H_5)_2Cl$.—Five grams of the carbinol were suspended in 50 cc. dry ether, the whole cooled to 0°, and dry hydrogen chloride passed in until all was in solution, and the solution thoroughly saturated with the gas. The deep red solution which resulted was dried over calcium chloride, filtered off, the filtrate concentrated and cooled to 0°. The chloride separated in elongated prisms, which were washed with dry ether and dried. Yield, 3 grams. Recrystallized from dry ether, colorless crystals were obtained, melting quite sharply at 110°.

0 5000 g. substance: 0 1928 g. AgCl Calcd for $C_{22}H_{21}O_3Cl$ Cl 9 63%. Found: Cl, 9 54%.

It is readily soluble in ligroin, ether or benzene; in alcohol it dissolves with hydrolysis. On standing in the air, it rapidly assumes a reddish color, as it is very sensitive to moisture. A small amount was shaken for a minute with water, filtered quickly, the filtrate acidified with nitric acid and silver nitrate added. A heavy precipitate of silver chloride resulted.

3,4,5-Trimethoxytriphenyl Methane, $(CH_3O)_3C_6H_2.CH(C_6H_5)_2$. -- Two grams of the carbinol were suspended in 15 cc. of absolute alcohol and dry hydrogen chloride passed in to saturation. The resulting deep red solution was heated for a short time under a reflux condenser, the alcohol distilled off, and the yellow residue purified by crystallization from alcohol. Fine, colorless needles were obtained, melting at 133°. Yield, 1.6 grams.

0 2334 g. substance: 0.6768 g. CO_2, 0.1411 g. H_2O Calcd for $C_{22}H_{22}O_3$ C 79.04%; H, 6 58%. Found, C, 78 88%; H, 6 71%.

It is insoluble in water, but readily soluble in alcohol, ether, chloroform or benzene.

This easy reduction of the carbinol was scarcely to be expected in the face of the results recorded by Kauffmann.[1] The latter found that when triphenylcarbinol was boiled for an hour with alcoholic hydrochloric acid, it was only partially reduced, and concluded from other results that a methoxyl group in the para position facilitated but little such a reduction, while in the meta position it had possibly a slight hindering effect.

In the above reduction, we observed no resinification.[2]

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[1] *Ber.*, 38, 2702 (1905); 41, 4423 (1908).

[2] Compare Kauffmann and Pannwitz, *Ber.*, 45, 766 (1912).

3,4,5-Trimethoxytriphenyl Pyrryl Methane, $(CH_3O)_3C_6H_2.C(C_6H_5)_2.C_4H_4N$.—Two grams of the carbinol and 0.7 gram of pyrrole were dissolved in 10 cc. of glacial acetic acid by warming, and the dirty green solution heated for 15 minutes under a reflux. On cooling, no crystals separated, so the acetic acid and excess of pyrrole were removed by distillation under diminished pressure, and the sticky green residue was extracted with boiling ligroin, considerable resinous material remaining undissolved. The ligroin extracts, on evaporation, deposited first some resin, and finally rosettes of white prisms of the pyrryl compound. These latter were separated mechanically and recrystallized from acetic acid, giving colorless hexagonal crystals, melting at 155° (uncorr.). Yield, 0.7 gram.

0.4263 g. substance: 12.45 cc. N_2 (21° and 763 mm, over H_2O). Calcd. for $C_{26}H_{25}O_3N$: N, 3.26%. Found· N, 3.35%.

The compound is readily soluble in alcohol, acetic acid, chloroform or benzene; less soluble in methyl alcohol or ligroin; and insoluble in water.

Attempts to avoid resinification by shorter boiling with acetic acid were unsuccessful, as complete condensation could not be accomplished in less than 15 minutes' heating, whereas much longer boiling caused entire resinification.[1]

3,4,5-Trimethoxy-α-methyl Styrene, $(CH_3O)_3C_6H_2.C(CH_3) : CH_2$.—38 grams of methyl iodide, dissolved in dry ether, were allowed to act upon 6.3 grams magnesium turnings. The reaction was vigorous, with nearly complete solution of the magnesium. When this reaction was over, a suspension of 20 grams of methyl trimethylgallate in 100 cc. of dry ether was added slowly. The mixture was allowed to stand for several hours, and the magnesium compound was then decomposed by ice and dilute sulfuric acid. The ethereal layer was separated, washed with water, dried over calcium chloride, filtered, and the filtrate evaporated. There remained a yellowish oil, which was probably the impure carbinol, since it was only partially volatile with steam, while the styrene itself is quite easily volatile.

All attempts to bring this oil to crystallization having failed, it was distilled under diminished pressure. At 193°, and a pressure of 40 mm., a colorless oil passed over and soon solidified to a colorless crystalline mass. Yield, 12 grams.

Some of this product was subjected to a steam distillation. It passed over completely, solidifying in the receiver to colorless needles, melting sharply at 37°. These were separated, dried and analyzed, with the following results:

0.2867 g. substance: 0.7249 g. CO_2, 0.2000 g. H_2O. Calcd. for $C_{12}H_{16}O_3$: C, 69.24%; H, 7.69%. Found: C, 69.09%; H, 7.74%.

The substance is readily soluble in alcohol, ether, acetone, acetic acid, chloroform, ligroin or carbon disulfide. In chloroform solution, it decolorizes the calculated amount of bromine, but on attempting to remove the solvent, hydrobromic acid is removed also, leaving a brown oily residue.

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[1] Compare Patzevitch, *Inaug. Dissert., Grenoble*, 1911.

This styrene is isomeric with the naturally occurring elemicin, and with the isoelemicin obtained by Semmler[1] by distilling elemicin over sodium.

3,4,5-Trimethoxy Acetophenone, $(CH_3O)_3C_6H_2.CO.CH_3$.—Six grams of the above styrene were dissolved in 25 cc. of 70% acetic acid, the solution placed in a Peligot tube, warmed to 50°, and ozone passed through it for four hours. The solution gradually assumed a deep reddish brown color, and the presence of formaldehyde in the escaping gases was indicated by the odor and by the Schiff reagent. The solution was then transferred to a distilling flask and subjected to distillation under diminished pressure. After the removal of the acetic acid, a light yellow oil distilled over at 220-4° and 40 mm. pressure. Some tar remained in the flask at the close of the distillation. The yellow oil soon solidified to a light yellow crystalline mass. Recrystallized from ligroin, it was obtained in colorless glistening needles, melting at 78°. Yield, 2.2 grams.

0.1976 g. substance: 0.4544 g. CO_2, 0.1171 g. H_2O. Calcd for $C_{11}H_{14}O_4$: C, 62.87%, H, 6.66%. Found, C, 62.70%, H, 6.59%.

This ketone was first obtained by Mauthner,[2] by the action of diazomethane upon trimethylgallic aldehyde, and also by the hydrolysis of trimethylgalloyl acetic ester. He describes it as melting at 72°, or 6° lower than our product. The identity of the two, however, was established by the preparation of the *p*-nitrophenyl hydrazone, which Mauthner describes as particularly characteristic. As prepared from our product, this derivative was found to agree in all respects with Mauthner's.

p-Nitrophenyl Hydrazone.—0.2 gram of the ketone was dissolved in 4 cc. of 50% acetic acid and a solution of 0.2 gram of *p*-nitrophenyl hydrazine in 4 cc. of 50% acetic acid was added. On warming, the hydrazone separated in brown needles, which were filtered off when the solution was cold, washed with dilute acetic acid, and recrystallized from alcohol, giving brown needles, melting at 195-6° (uncorr.).

3,4,5-Trimethoxy Chalkone, $(CH_3O)_3C_6H_2.CO.CH : CH.C_6H_5$.—Half a gram of the above acetophenone and 0.25 gram of benzaldehyde were dissolved in 10 cc. of alcohol, and 2.5 cc. of 45% potassium hydroxide solution added. On standing for some time, yellow needles began to separate from the solution. The mixture was left over night, and the separated chalkone then filtered out, washed, and recrystallized from alcohol. Pale yellow needles were obtained, melting at 78-8.5°. Yield, 0.4 gram.

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[1] *Ber.*, **41**, 1769, 1918 (1908).

[2] *J. prakt. Chem.*, [2] **82**, 275 (1910).

0.1297 g. substance: 0.3447 g. CO_2, 0.0704 g. H_2O. Calcd. for $C_{18}H_{18}O_4$: C, 72.49%; H, 6.03%. Found: C, 72.46%; H, 6.04%.

Bargellini and Avrutin[1] have prepared recently the isomeric 2,4,5-trimethoxy chalkone.

3,4,5-Trimethoxyphenyl Diethyl Carbinol, $(CH_3O)_3C_6H_2.C(C_2H_5)_2.OH$.—The necessary Barbier-Grignard reagent was prepared from 6.3 grams of magnesium turnings and 29 grams of ethyl bromide in dry ether. It was acted on by 20 grams of methyl trimethylgallate suspended in 100 cc. of dry ether. After the first vigorous reaction was over, the mixture was allowed to stand for four hours. The magnesium compound was then decomposed, as usual, with ice and dilute sulfuric acid, the ether layer separated, washed with water, dried over calcium chloride, and evaporated to dryness. A light yellow oil remained which partly solidified to a crystalline mass. These crystals were separated, washed with ligroin, and recrystallized from ligroin. As thus obtained, they formed beautiful, blunt, colorless needles, melting at 74°, and decomposing with loss of water at 147°. Yield, 6 grams.

0.1995 g. substance: 0.4831 g. CO_2, 0.1543 g. H_2O. Calcd. for $C_{14}H_{22}O_4$: C, 66.15%; H, 8.68%. Found: C, 66.03%; H, 8.60%.

The substance is easily soluble in methyl or ethyl alcohol, ether, acetone, chloroform, benzene or toluene; moderately soluble in ligroin; insoluble in water. It is quite unstable and passes into the olefin so readily that its isolation and purification were matters of considerable difficulty. In decomposing the above magnesium compound there was always obtained a mixture of the carbinol and olefin.

3-(3,4,5-Trimethoxyphenyl)-pentene(2), $(CH_3O)_3C_6H_2.C(C_2H_5):CH.CH_3$, was separated in quantity from the mother liquors from the crystallization of the preceding carbinol. These ligroin mother liquors were combined, the ligroin distilled off, and the residual yellow oil distilled under diminished pressure. At 210–20° and 40 mm. pressure, a pale yellow oil passed over. On rectification, the oil was obtained practically colorless, and of the same boiling point as before. Yield, 12 grams.

This olefin resulted also from the following experiment: three grams of the carbinol were dissolved in 30 cc. of ether, the solution cooled to 0° and saturated with dry hydrogen chloride. The ether was then removed at low temperature, the residue taken up with fresh ether, dried over calcium chloride, and the ether again evaporated. This residue contained no chlorine, and proved to be identical with the pentene described above.

The following analyses and experiments were conducted with the product of the first method of preparation.

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[1] *Gazz. chim. ital.*, 40, II, 346 (1910).

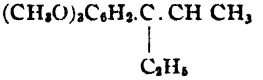
0.2739 g. substance: 0.7121 g. CO_2, 0 2057 g. H_2O. Calcd. for $C_{14}H_{20}O_3$: C, 71.19%; H, 8 47% Found: C, 70 82%; H, 8.35%.

The substance is easily soluble in alcohol, ether, ligroin, chloroform or benzene; insoluble in water; $n_D^{20} = 1.53600$; $d_0 = 1.0462$.

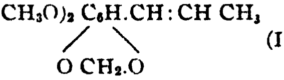
From the equation

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d_t} = MR,$$

the observed molecular refraction is 70.37; while that calculated from the Brühl-Conrady tables is 67.9. The compound thus shows an exaltation in molecular refraction of 2.47, corresponding rather closely to the exaltation of 2.3 shown by isapiol,[1] a body of somewhat similar structure:



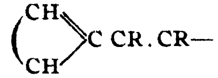
$$(CH_3O)_3C_6H_2.\underset{\displaystyle C_2H_5}{\underset{|}{C}}.CH\ CH_3$$



$$(CH_3O)_2\ \underset{\displaystyle O\ CH_2.O}{\underset{/\ \ \backslash}{C_6H}}.CH:CH\ CH_3$$

(Isapiol)

It should be noted that this exaltation is considerably greater than was to have been expected from the observation of Eisenlohr,[2] who states that the exaltation from a molecule of the general structure



lies in the neighborhood of 0.45.

The behavior of this olefin with bromine is much like that of the styrene already described. Two grams of the pentene and the calculated amount of bromine were brought together in chloroform solution. The bromine was absorbed and the solution remained momentarily colorless; but on standing hydrobromic acid was given off quite rapidly, the color of the solution passing through reddish violet to a final dirty green. On evaporating the chloroform, there remained a dark green oily residue which was not further examined.

3,4,5-Trimethoxy Propiophenone, $(CH_3O)_3C_6H_2.CO.C_2H_5$.—Eight grams of the above pentene were dissolved in 25 cc. of 70% acetic acid and ozone passed through the warm solution for four hours. A deep reddish brown solution resulted, and the presence of acetic aldehyde was indicated in the escaping gases. This solution was then distilled under reduced pressure. After the removal of the acetic acid, a heavy yellow oil passed over at 210° and 40 mm. This oil solidified to a brownish crystalline mass on standing. It was recrystallized from ligroin and then appeared in glistening colorless needles, melting at 53.5°. Yield, 3.4 grams.

0.2014 g. substance: 0.4740 g. CO_2, 0 1290 g. H_2O. Calcd. for $C_{12}H_{16}O_4$: C, 64 30%; H, 7 14% Found: C, 64 19%; H, 7.15%.

The compound is easily soluble in alcohol, ether, chloroform, acetic acid or benzene; moderately soluble in ligroin; insoluble in water.

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[1] Eykmann, *Ber.*, 23, 863 (1889).

[2] "Spectrochemie organischer Verbindungen," Stuttgart, 1912.

p-Nitrophenyl Hydrazone.—0.2 gram of the above ketone and a similar amount of *p*-nitrophenyl hydrazine were each dissolved in 4 cc. of 50% acetic acid, the two solutions mixed and the mixture warmed for 30 minutes at 100°. The hydrazone separated in dark reddish brown crystals. When the solution had been thoroughly cooled, the separated hydrazone was filtered out, washed with acetic acid, and recrystallized from alcohol. It was thus obtained in dark reddish brown needles, somewhat resembling chromic anhydride, and melting at 183–4°. Yield, 0.22 gram

0.1627 g. substance: 16.65 cc. N_2 (21° and 773 5 mm. over H_2O). Calcd. for $C_{18}H_{21}O_6N_3$: N, 11.70%. Found: N, 11.57%.

4 - (3,4,5 - Trimethoxyphenyl) - heptene(3), $(CH_3O)_3C_6H_2.C(CH_2.C_2H_5):$-$CH.C_2H_5$.—The necessary Barbier-Grignard reagent was prepared from 6.3 grams of magnesium turnings and 40 grams of normal propyl iodide, and 20 grams of methyl trimethylgallate were condensed with it in the manner already described in the preceding pages. The magnesium compound was decomposed with ice and dilute sulfuric acid, the ether layer separated, washed, dried, and evaporated. The light yellow oil which remained could not be crystallized, so it was distilled under diminished pressure. It distilled almost completely at 215–8° at 40 mm. pressure, as a pale yellow oil.

0.1877 g. substance: 0.5001 g. CO_2, 0 1530 g. H_2O. Calcd. for $C_{16}H_{24}O_3$: C, 72.72%; H, 9 09%. Found. C, 72 68%; H, 9.06%.

$n_D^{20} = 1.52877$; $d_{20} = 1.0300$. Molecular refraction: observed, 79.12; calculated, 77.12. Here, too, considerable exaltation is evident.

The heptene dissolves in alcohol, ether, ligroin, acetic acid, chloroform or benzene; but is insoluble in water. With bromine, it shows a behavior similar to that of the pentene already described.

No carbinol at all was encountered among the products of the above reaction.

3,4,5-Trimethoxy Butyrophenone, $(CH_3O)_3C_6H_2.CO.CH_2.C_2H_5$.—Seven grams of the above heptene were dissolved in 35 cc. of dilute acetic acid, the solution warmed, and ozone passed through it for 15 hours, by which time it no longer decolorized a bromine solution. The solution was then subjected to distillation under reduced pressure. After the acetic acid was removed, a heavy, yellow oil distilled over at 218–20° and 40 mm. pressure. This oil slowly solidified to a crystalline, somewhat oily mass. Yield, 4.5 grams.

Great difficulty was experienced in purifying this ketone, as it is easily soluble in methyl or ethyl alcohol, ether, chloroform, carbon tetrachloride, ligroin, carbon disulfide, acetone, ethyl acetate, ethyl bromide, pyridine, benzene or toluene. From dilute methyl alcohol, or dilute acetic acid, it tends to separate as an oil. It was finally obtained in long, colorless needles from dilute methyl alcohol, melting at 51–52.5°, which were still somewhat impure.

p-Nitrophenyl Hydrazone.—Equal weights (0.5 gram of each) of the ketone and of *p*-nitrophenyl hydrazine were each dissolved in 10 cc. of 50% acetic acid, the solutions mixed, and the mixture warmed at 100° for 30 minutes. A heavy, red oil separated and gradually solidified to a crystalline mass. The separated hydrazone was removed, washed with dilute acetic acid, and recrystallized from alcohol. Dark brownish red needles were obtained, melting sharply at 160°. Yield, 0.6 gram.

0.1263 g. substance: 13 1 cc. N_2 (21 5° and 756 mm over H_2O). Calcd. for $C_{19}H_{23}O_6N$: N, 11 26%. Found: N, 11 40%.

5-(3,4,5-Trimethoxyphenyl)-2,8-dimethylnonene(4), $(CH_3)_2CH.CH_2.CH:C[C_6H_2(OCH_3)_3]CH_2.CH_2.CH(CH_3)_2$.—The reaction was carried out in the usual way, employing 6 grams of magnesium turnings, 47 grams of isoamyl iodide, and 18 grams of methyl trimethylgallate. After decomposing the magnesium compound with ice and dilute sulfuric acid, the ether layer was separated, washed, dried, and evaporated. A yellow oil remained which deposited a few crystals on standing. The addition of ligroin caused a considerable increase in the quantity of these crystals. They were filtered out, washed with ligroin and dried. Yield, 3.5 grams. Recrystallized from benzene, the substance was obtained in colorless rhombohedral crystals, melting at 109–10°, and showing no sign of decomposition at 265°. It distils unchanged at 218° and 40 mm. pressure.

I. 0.2003 g. substance: 0.4148 g. CO , 0 1117 g. H_2O.
II. 0.1983 g. substance: 0 4103 g. CO_2, 0.1031 g. H_2O.
III 0.1914 g. substance: 0.3981 g. CO_2, 0 1000 g. H_2O.

Found.	Carbon, %.	Hydrogen, %	Oxygen, %.
I	56.48	6 19	....
II	56.98	5 77	....
III	56 74	5.79	....
Average	56 72	5.92	37.36

Analysis I was run on undistilled material, II and III on the distilled.

These results correspond quite closely to the formulas $C_{12}H_{14}O_6$ and $C_{12}H_{16}O_6$:

	Carbon.	Hydrogen.	Oxygen.	M. W
$C_{12}H_{14}O_6$	56.7	5.5	37 8	254
$C_{12}H_{16}O_6$	56.3	6.2	37.5	256

Cryoscopic molecular-weight determinations in benzene solution gave the following results:

I. 0.5026 gram undistilled material, in 17.5735 grams benzene, gave a freezing-point depression of 0.629°. Super-cooling = 0.43°. M. W. = 228.5.

II. 0.5005 gram distilled material, in 17.5735 grams benzene, gave a freezing-point depression of 0.537°. Super-cooling = 0.21°. M. W. = 260.6.

Average of the above determinations, 244.6.

The substance is easily soluble in alcohol, ether, chloroform, or benzene, difficultly soluble in ligroin or water. Its aqueous solution is neutral to indicators, and with dilute neutral potassium permanganate solution in the cold is entirely consumed. It does not decolorize a chloroform solution of bromine. Warmed with phosphorus pentachloride, a reaction occurs. Attempts to form an oxime or a phenylhydrazone failed. The identity of the compound is still undisclosed.

The nonene itself was found in the ligroin mother liquors from the above crystals. It is the chief product of the reaction, no carbinol having been encountered. These ligroin mother liquors were evaporated to dryness and the residual yellow oil distilled under diminished pressure. At 235–7° and 40 mm., a light yellow oil passed over. Yield, 12 grams.

0 2224 g. substance: 0 5930 g. CO_2, 0 1949 g H_2O Calcd. for $C_{20}H_{32}O_3$ C, 72 72%; H, 9 69%. Found, C, 72 71, H, 9 71%.

Observed molecular refraction, 96.03; molecular refraction as calculated from the Brühl-Conrady tables, 95.53. This exaltation of 0.50 agrees quite closely with the figure of 0.45 found by Eisenlohr[1] for compounds of this type.

The action of bromine upon a chloroform solution of the nonene was similar to that recorded for the preceding olefins. An attempt to split the nonene with ozone, in the hope of getting the corresponding valerophenone, was discontinued because the oxidation proceeded so slowly that even after passing ozone through the solution for 20 hours, it still decolorized bromine.

3,4,5-Trimethoxyphenyl Dibenzyl Carbinol, $(CH_3O)_3C_6H_2.C(CH_2.C_6H_5)_2.$-OH.—The reaction was carried out as described for the other carbinols, using 6.5 grams magnesium turnings, 35 grams benzyl chloride and 20 grams methyl trimethylgallate, in presence of dry ether. After decomposing the magnesium compound with ice and dilute sulfuric acid, the ether layer was separated, washed with water, dried with calcium chloride, and concentrated. On cooling, the carbinol separated practically pure. Recrystallized from methyl alcohol, it formed elongated prisms, melting at 116–7°. Yield, 22 grams.

0 2011 g. substance. 0 5611 g. CO_2, 0.1245 g. H_2O. Calcd. for $C_{24}H_{26}O_4$: C, 76 2%; H, 6 88%. Found: C, 76 11%; H, 6 88%.

It is readily soluble in methyl or ethyl alcohol, chloroform or benzene, sparingly soluble in ligroin or ether, and insoluble in water. Unlike most of the carbinols described in the foregoing pages, this one is quite stable, showing no tendency to decompose even when heated above 350°.

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[1] *Loc. cit*

3,4,5-Trimethoxy-α-benzyl Stilbene, $(CH_3O)_3C_6H_2.C(CH_2.C_6H_5) : CH.C_6H_5$.—Ten grams of the carbinol were suspended in 50 cc. of dry ether, the whole cooled to 0° and saturated with dry hydrogen chloride. The carbinol dissolved. After allowing the resulting colorless solution to stand for a few minutes, the ether and hydrogen chloride were evaporated at low temperature, the residue dissolved in fresh ether, this ether solution dried with calcium chloride, and the ether driven off again. A viscous light yellow oil remained which, after standing for several weeks, finally crystallized. Recrystallized from ligroin, it formed colorless rhombohedral crystals, which melted sharply at 93°. Yield, 8 grams.

This product, instead of proving to be the expected chloride, turned out to be the stilbene. It contained no chlorine.

0.2003 g substance: 0.5841 g CO_2, 0.1193 g H_2O. Calcd for $C_{24}H_{24}O$ C, 80.00%; H, 6.67% Found C, 79.67%, H, 6.62%

It is readily soluble in alcohol, ether, chloroform, carbon disulfide or benzene, moderately soluble in ligroin or pyridine, insoluble in water. It distils with slight decomposition at 320° under a pressure of 20 mm.

When this stilbene and the calculated amount of bromine were brought together in chloroform solution, the color of the bromine immediately disappeared, but on attempting to evaporate the chloroform there was a copious evolution of hydrogen bromide and only a cherry-red tar remained.

In view of the considerable stability of the carbinol, and the evident instability of the dibromide, the production of the stilbene in the above reaction is probably to be ascribed to the intermediate formation of the chloride, with subsequent elimination of hydrogen chloride.

3,4,5-Trimethoxy Desoxybenzoin, $(CH_3O)_3C_6H_2.CO.CH_2.C_6H_5$.—Five grams of the stilbene were dissolved in 35 cc. of 70% acetic acid,[1] the solution transferred to a Peligot tube immersed in a bath at 70°, and ozone passed through it for three hours. The solution gradually turned a reddish brown color and a strong odor of benzaldehyde was noticed. The acetic acid was finally distilled off under diminished pressure and the brown residue crystallized from methyl alcohol. Beautiful, colorless needles were obtained, melting sharply at 99°. Yield, 2 grams.

0.1994 g. substance: 0.5223 g CO_2, 0.1129 g H_2O. Calculated for $C_{17}H_{18}O_4$ C, 71.32%; H, 6.29%. Found: C, 71.42%; H, 6.29%

It is readily soluble in methyl or ethyl alcohol, ligroin, ether, chloroform or acetic acid, but is insoluble in water.

p-Nitrophenyl Hydrazone.—This was prepared by separately dissolving equal amounts (0.2 gram of each) of the ketone and of *p*-nitrophenyl hydrazine, each in 4 cc. of 50% acetic acid, mixing these solutions and warming the mixture. The hydrazone separated in orange needles. When the mixture had cooled thoroughly, the crystals were filtered out, washed with dilute acetic acid, and recrystallized from alcohol. Fine orange needles resulted, which sintered at 185° and gave a clear melt at 194.° Yield, 0.19 gram.

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[1] Compare Otto, *Ann. chim. phys.*, [8] 13, 77 (1908), D. R. P. No. 97,620

0 1147 g. substance. 10 15 cc N_2 (21° and 773 5 mm. over H_2O). Calcd for $C_{23}H_{23}O_5N_4$: N, 9 97%. Found: N, 10 00%

3. Summary.

1. The study of methoxylated carbinols has been extended by an investigation of a series of carbinols obtained by the action of various magnesium reagents upon trimethylgallic ester.

2. The 3,4,5-trimethoxytriphenyl carbinol has been found to be more strongly basic than triphenyl carbinol, but less so than *p*-methoxytriphenyl carbinol.

3. The trimethoxyphenyl dialkyl carbinols are generally unstable, losing water readily to form the olefin; whereas the trimethoxyphenyl dibenzyl carbinol is quite stable.

4. The action of isoamyl magnesium iodide upon trimethylgallic ester appears to follow a somewhat abnormal course, giving an unidentified by-product, in addition to the olefin.

5. Trimethoxyphenyl-diethyl and -dibenzyl methyl chlorides are very unstable.

6. A series of olefins of the type $(CH_3O)_3C_6H_2.CR : CHR$ have been prepared, and it has been shown that these substances do not form stable dibromides. Certain of these hydrocarbons show marked exaltation in molecular refraction.

7. A series of new 3,4,5-trimethoxyphenyl ketones has been obtained and examined.

8. New syntheses are recorded of 3,4,5-trimethoxy cinnamic acid, of syringic acid and of 3,4,5-trimethoxy acetophenone.

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NEW YORK.

SOME ORGANIC PREPARATIONS.

BY L. P. KYRIAKIDES.

Received January 2, 1914.

During the past three years we have had the occasion to use many organic reactions, and as the result of our study, we have been able to improve some of them.

The substances prepared and described are mainly related to the synthesis of the unsaturated hydrocarbons with conjugated double bonds, which of late years have become so important in the synthetic production of rubber-like masses.

Aldols.—These compounds have been known for quite a long time. They are usually prepared by condensing the aldehydes alone, or in mixture with other aldehydes, by means of alkaline bodies, especially carbonates. The best method known is that described by Grignard and Abelmann,[1] which consists in treating an ethereal solution of an aldehyde or a mixture of aldehydes with a solution of potassium hydroxide and stirring in the cold.

Acetbutyraldol, $CH_3.CH(OH).CH(CH_2.CH_3).CHO$.—This substance, as far as known to us, has not been prepared before. It is easily prepared by Grignard and Abelmann's[2] method. 160 g. freshly prepared acetaldehyde and 250 g. freshly distilled normal butyraldehyde are dissolved in 600 cc. ether. The solution is cooled to below 5° and treated slowly, while the condensation liquid is being stirred vigorously, with a 10% solution of potassium hydroxide. In all, about 70 cc. of the alkaline solution are used, the addition of which takes about 45 minutes. The liquid is stirred during the condensation continuously, and the temperature of the reaction mixture is never allowed to go above 10°. A good temperature is 5–7°. When it is observed that the liquid has no appreciable tendency to warm up, the reaction is assumed to be at an end. The aldol solution is separated from the alkaline layer, shaken several times with a little saturated sodium bicarbonate solution and dried over calcium chloride. After evaporating off the ether, the residue is distilled *in vacuo* from an oil bath. We have thus obtained 214 g. acetbutyraldol, boiling up to 110° at 24 mm. A redistilled sample boiled at 102–104° in the neighborhood of 20 mm. Acetbutyraldol is insoluble in water, but dissolves readily in ether and alcohol.

Acetaldol, $CH_3.CHOH.CH_2.CHO$.—This substance is easily obtained by using Grignard and Abelmann's method, although these authors have not described its preparation. In another article, Grignard and Reif[3] describe the preparation of acetaldol by treating an ethereal solution of acetaldehyde with an aqueous solution of sodium sulfite in the cold. In Grignard and Abelmann's process, which we have applied to the preparation of acetaldol, the results were excellent—the temperature of condensation being about 7°. Using acetone as diluent instead of ether, we have obtained very good yields of exceptionally good aldol. It might be supposed that in this latter condensation there might be some hydracetylacetone also formed, by the interaction between acetaldehyde and the acetone. On decomposing the aldol into the unsaturated derivative however, we could obtain very little, if any, ethylidene acetone, which tends to prove that in this condensation there is no appreciable formation of hydracetylacetone. The amount of acetone used as diluent was less than twice the volume of acetaldehyde taken.

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[1] *Bull. soc chim.*, [4] 7, 638 (1910)

[2] *Ibid*

[3] *Bull. soc chim.*, [4] 1, 114.

In our further study of the aldol condensations, we have been able to dispense with the use of solvents altogether.

One of the drawbacks in these condensations is the fact that the aldehydes and aldols are usually very sensitive towards the alkalies, so that there is more or less resinification during the reaction. The older experimenters avoided this trouble, partially, by using weak alkaline compounds to effect the condensation; while of late the tendency has been to use strong alkalies in presence of inert organic solvents, which latter extracted continually the sensitive compounds from the sphere of action of the alkali.

It is noted by many that, in carrying out these condensations, the end of the reaction is judged by the appearance of a light yellow color in the aldol liquid. It has been our experience that this color is a sign of the formation of higher condensation products and resins. For a good aldol formation it is necessary that the liquid should be perfectly colorless.

A. F. McLeod,[1] in a paper on the condensation of acetaldehyde with formaldehyde states: "With calcium or sodium hydroxide solution of 0.1% either no condensation, or, only a very slow condensation of acetaldehyde occurred."

We have found, however, that it is very easy to condense acetaldehyde to acetaldol with amounts of sodium hydroxide equivalent to about 0 1 0.3% of the aldehyde used.

1 kilo freshly prepared acetaldehyde, in a long-necked 2-liter flask, is cooled to below 5°. The thermometer bulb must be within the liquid to be condensed, and the temperature carefully controlled during the reaction. To the cold acetaldehyde are now carefully added 5 cc. of a 10% sodium hydroxide solution, and the condensation carried on at 4–5°. The reaction mixture must be kept in brisk motion during the whole of the operation. After a short time, 5 cc. more of the alkali are added, and the process repeated, until in all about 20–25 cc. of the 10% sodium hydroxide solution have been added. This is perfectly soluble in the aldehyde-aldol. The addition takes about 20 minutes. The reaction liquid is then kept shaking at 4–5° for an hour more, after which it is made slightly acid with tartaric acid. The aldol is filtered from the salt, and distilled *in vacuo* from an oil bath, whose temperature is raised slowly. It was thus easy to obtain about 50% of the theoretical yield of acetaldol, the boiling point of which, on redistillation, was found to be 80° at 20 mm., and 72° at 12 mm. Part of the aldol is decomposed back into acetaldehyde during the distillation, as it has often been observed; otherwise the yield in non-distilled aldol varies between 70–80%

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[1] *C. A.*, 1, 717 (1907).

of the theoretical. It may be possible by increasing the time of reaction to obtain higher yields of aldol. The side products, such as higher condensation products and resins, do not amount to more than 1% of the aldehyde used, neither is there any crotonaldehyde formed. It might be noted here that the addition of some organic solvent, such as ether, facilitates the filtration of the aldol from the sodium tartrate.

For the control of the temperature during the condensation of the acetaldehyde it is advisable to have a freezing mixture ready. For most reactions it is not necessary to distil the aldols; it is sufficient to separate them from the free aldehydes by heating them for a short time *in vacuo.* As the rate of aldol condensation is a function of the concentration of the alkali, it stands to reason that the time of reaction can be varied by varying the amount of alkali used. In fact, an experiment with 0.12% of sodium hydroxide– percentage on the basis of aldehyde used– –gave only 34% of distilled aldol, during a reaction of about one hour.

The method described above would be applicable to the preparation of the higher members of the series as these are, according to Grignard and Abelmann, relatively more stable in presence of the alkalies.

Unsaturated Aldehydes and Ketones.

These substances are usually obtained as by-products in the corresponding aldol condensations. They are also formed on heating the hydroxyaldehydes or hydroxy-ketones. We have been able to simplify the dehydration of these last named substances by generalizing known methods. The dehydration is effected by heating the aldol compounds with traces of a strong acid such as sulfuric acid or substances generally known as dehydrating catalytics, such as aluminum phosphate.

Crotonaldehyde, $CH_3.CH : CH.CHO$.—M. Delépine's[1] method of preparing this substance by treating paraldehyde with concentrated sulfuric acid is not very attractive. The method described by Grignard and Reif,[2] which consists in heating aldol in a flask provided with a column, is extremely slow and consequently tiresome. As a rule, the preparation of crotonaldehyde has not been very easy. Using, however, a catalyst, aldol can be easily dehydrated into crotonaldehyde.

The crude aldol from about 2500 g. acetaldehyde was put in a three-liter flask provided with an eight-bulb Young's column. The aldol was then treated with about 10 g. powdered aluminum phosphate and heated to boiling. The decomposition products boiling above 80° were collected for crotonaldehyde. The lower fractions contain acetaldehyde. The temperature of the distilling vapors soon attained the maximum of 100–105°. No appreciable residue was left in the flask, which, if present, is due to the resins formed in the aldol condensation.

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[1] *Compt. Rend.,* **147,** 1316 (1908).

[2] *Bull. soc. chim.,* [4] **1,** 114.

The distillate was saturated with calcium chloride, the organic liquid dried quickly over calcium chloride and fractioned through a column. We have been able to obtain 1225 g. crotonaldehyde, boiling at 98–102° C., or about 60% of the theoretical yield on the acetaldehyde originally used. It is easy by this method to dehydrate over a kilo of aldol in less than three hours.

Ethylidene Acetone, $CH_3.CH : CH.CO.CH_3$.—This substance also is said to be formed on long heating of hydracetylacetone. It is also obtained on heating the latter substance with acetic anhydride.[1] It is easily prepared catalytically:

400 g. hydracetylacetone—$CH_3.CH(OH).CH_2.CO.CH_3$—are treated with two drops of concentrated sulfuric acid and distilled from a flask provided with a column. The distilling vapors attain the maximum temperature of about 120° There is some acetone and acetaldehyde in the low boiling fractions. The distillate is treated with potassium carbonate, the organic layer dried over the same drying agent and fractioned through a column. Ethylidene acetone boils at 122°. In a similar way mesityl oxide can be prepared from diacetone alcohol by using aluminum phosphate or better still, sulfuric acid—a few drops of the acid to a kilo of the ketone alcohol (compare Moritz Kohn).[2]

The diacetone alcohol we have prepared by using barium hydroxide as the condensing agent. The alkali was put in a Soxhlet apparatus and the acetone boiled on a steam bath for several days until the liquid stopped boiling. A little tartaric acid was added to the acetone at the beginning of the reaction, in order to neutralize any barium hydroxide carried down from the Soxhlet apparatus, either mechanically or in solution. A. Hoffman[3] uses calcium hydroxide for condensing acetone to diacetone—alcohol. Barium hydroxide being a stronger alkaline substance, comparable in its alkalinity to the alkali hydroxides, increases the rate of condensation.

Glycols of the Hydrocarbons.

These substances are usually prepared by the reduction of the corresponding hydroxy-aldehydes and hydroxy-ketones with aluminum amalgam. In some cases they have been prepared by the reduction of ketone alcohols with sodium amalgam. We have discovered that dihydroxyl compounds can be easily obtained by the electrolytic reduction of the corresponding aldol bodies. Since our discovery, we have seen a patent,[4] assigned to the Farbenfabriken of Elberfeld, which deals with a method identical with ours. The reduction is effected as follows:

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[1] *Ber.*, **25**, 3166.

[2] *Chem. Zentr.*, **1913**, II, 577

[3] THIS JOURNAL, **31**, 722.

[4] Eng. Pat. 940 of Jan. 13, 1913; see also *C. A.*, **7**, 3242 and *Soc. Chem. Ind.*, **1913**, 550.

Butandiol-1,3, $CH_3.CH(OH).CH_2.CH_2OH$.—Twenty-five grams of acetaldol, distilled *in vacuo*, were dissolved in 100 cc. of water, and then treated with a cold solution of 10 cc. concentrated sulfuric acid in 20 cc. of water. The solution thus made served as the cathode liquid and was poured within the porous cup of an electrolytic cell. The anode liquid consisted of a 10% aqueous sulfuric acid. The electrodes were made of lead. The cathode consisted of a spiral through which cold water was kept running. The effective cathode surface was 125 cm^2. The aldol solution within the porous cup was kept in motion by a mechanical stirrer moving within the loops of the lead spiral. The temperature of the cathode liquid during electrolysis was below 15°. The aldol solution was electrolyzed for 4 hours and 30 minutes, at a potential of 4 volts and a current strength of about 6 amperes—ND_{100} = 5 amperes. After electrolysis the cathode liquid was neutralized and saturated with potassium carbonate, and extracted five times with a mixture of ether and alcohol. The ether-alcoholic solution was dried over potassium carbonate, the solvents distilled off and the residue fractioned *in vacuo*. We collected 18 g. substance boiling between 105 and 120° at 20 mm. The major portion of the glycol distilled over at 110–114° at the same pressure. The total high boiling residue was less than 2 g. The glycol, distilled at ordinary pressures, boiled at about 205°. The yield of glycol was therefore nearly 70% of the theoretical. For most purposes, the crude aldol, obtained after treatment *in vacuo* to free it from acetaldehyde, can be electrolyzed directly in a 10–15% aqueous sulfuric acid as a 20% aldol solution. The yields vary between 40–50% of the theoretical.

Ketone alcohols can be reduced in a similar manner to the corresponding dihydroxy-compounds. Thus, an aqueous solution of crude methyl-2-butanon-3-ol-1, made by the condensation of methylethylketone with formaldehyde, gave about 35% of methyl-2-butandiol-1,3, on electrolyzing in a 10% sulfuric acid solution, as with acetaldol.

Aldols are also easily reduced to the glycols in a manner similar to Zelinsky and Ujedinoff's[1] reduction of hydracetylacetone to pentandiol-2,4. The acetaldol, being reduced in this way, gave over 80% of pure butandiol-1,3.

Pinacone, $(CH_3)_2C(OH).C(OH)(CH_3)_2$.—This substance is easily prepared by the methods of Holleman,[2] or Richard and Langlais,[3] which consist in treating acetone with magnesium amalgam.

As calcium is so closely allied to magnesium in many of its reactions, we have attempted to reduce acetone to pinacone with calcium amalgam. As, however, calcium oxide is a strongly alkaline substance as compared with magnesium oxide, the side products obtained in the reduction are more abundant. H. D. Law and F. M. Perkin[1] have observed that metallic calcium acting on acetone at ordinary temperatures induces the formation of mesityl oxide together with higher condensation products. At higher temperatures the amount of high condensation products increases correspondingly.

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[1] *J. prakt. Chem.*, **84**, 545 (1911).

[2] *Rec. trav. chim.*, **25**, 206 (1906).

[3] *Bull soc. chim.*, [4] **7**, 454 (1908).

43 g. calcium were amalgamated with 800 g. mercury. The amalgamation required long heating because of a layer of calcium oxide on the surface of the metal turnings. The cold calcium amalgam was treated with 400 cc. of acetone and the mixture boiled for more than 24 hours on the steam bath. The flask was shaken occasionally in order to break the amalgam. Because of this massive lump the amalgam had not all reacted. The reaction mixture was treated with 45 g. water, boiled, filtered, and the precipitate extracted twice with boiling acetone. The liquid was distilled until the vapors attained the temperature of 95°. The residue was treated with 100 cc. water, inoculated with a crystal of pinacone hydrate and left in the ice-chest. The liquid was filtered off from the crystals, the latter were washed with cold water, then with benzol and dried by pressing between filter papers. The pinacone hydrate thus obtained weighed about 50 g. The yield of the substance was therefore more than 20% of the theoretical.

We have tried to carry out this reduction in presence of an inert organic solvent but the results were poorer, if anything.

Because of the relative cheapness of production of calcium as compared with magnesium, the study of this reduction of acetone with calcium amalgam to pinacone might be worth while.

Conclusions.

Aldol condensations can be effected by means of the alkali hydroxides, even in the case of aldehydes which are very sensitive towards these hydroxides. Where weak alkalies have heretofore been used, these can be replaced by the alkali hydroxides, only in the latter case the amount of the condensing agent must, naturally, be much smaller. The relative amounts of the different alkalies can be determined by comparing their dissociation constants.

Aldols and ketone alcohols can be reduced to the corresponding dihydroxy-compounds electrolytically in a sulfuric acid solution, preferably at a lead cathode, or in a way similar to Zelinsky and Ujedinoff's reduction-method of hydracetylacetone to pentandiol-2,4.

Pinacone can be obtained by the reduction of acetone with calcium amalgam.

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[1] *Chem. Zentr.*, 1908, (I), 1610.

In conclusion, I wish to express my thanks and indebtedness to my colleague, R. B. Earle, for assistance in the study of these reactions and many valuable suggestions

CAMBRIDGE, MASS.

THE PREPARATION OF DIGLYCERIDES.[1]

By R. R. Renshaw.

Received January 2, 1914.

The preparation and isolation of the diglycerides is an unusually difficult task, for several reasons. In the most fruitful methods of preparation, there is always obtained a mixture of the di- and triglycerides, as well as free fatty acids and possibly small quantities of the isomeric diglycerides.[2] These products do not differ greatly in solubility or crystallizability, and some of them are exasperatingly alike in these properties. The melting points of all of them are close together, and some have double melting points. The problem is complicated, too, on account of considerable disagreement in the data afforded by the literature.[3]

The following methods for the preparation of the 2,3-diglycerides are theoretically possible:

1. By the direct action of the fatty acid on glycerol or the monoglycerides at higher temperatures.[4] It has been supposed that the 1,3-

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[1] Presented in part at the forty-fifth general meeting of the American Chemical Society, Washington, D. C., Dec. 28, 1911.

[2] It is possible that the diglyceride may also form with the free acid present stable double compounds. Grün and Schacht (*Ber.*, **40**, 1786 (1907)), have isolated from the action of myristic acid on glyceryl disulfate a compound to which they have assigned the formula $C_3H_5(OH)(OCOC_{13}H_{27})_2 + 2C_{13}H_{27}COOH$.

[3] A typical example is illustrated in the glycerides of stearic acid

Stearic acid melts at 69.2°. It is readily soluble in ethyl ether, and in cold petroleum ether.

1-Monostearin melts at 73° (Guth, *Z. physiol. Chem.*, **26**, 83 (1902)); 78° (Kraft, *Ber.*, **34**, 4343 (1903)). It is sparingly soluble in cold ethyl ether and in cold petroleum ether.

2,3-Distearin melts at 72.5° (Guth); 76° and remelts at 58°, and after several months' standing at 74.5° (Grün, *Ber.*, **36**, 2286 (1905)); **38**, 1781 (1907)); 76.5° (Hundeshagen, *J. prakt. Chem.*, **28**, 219). It is sparingly soluble in cold ethyl ether and in cold petroleum ether.

1,3-Distearin melts at 74.5° (Guth); 78.2° (Grun and Theimer, *Ber.*, **38**, 1995 (1907)). The author has confirmed the latter. This glyceride is sparingly soluble in cold ethyl ether, and in cold petroleum ether

Tristearin melts at 71 to 71.5° and remelts at 55° (Guth) It is sparingly soluble in cold ethyl ether, and in cold petroleum ether.

The same relationship as regards solubility holds for these substances in other solvents.

[4] For the preparation of the stearins by this method, see Berthelot, Vol. 2, p. 67; Hundeshagen, *J. prakt. Chem.*, **28**, 227 (1883).

diglyceride was the one always formed by this method to the exclusion of the 2,3-modification. The writer, however, feels certain that at least a small amount of the 2,3-isomer has been obtained by means of this procedure by Hundeshagen.[1] In addition to these two isomers, there is always present varying amounts of free acid and the mono- and triglycerides. This mixture gives extreme difficulty in its separation, and it was not investigated.

2. By the double decomposition between 2,3-dihalide propanol and two molecules of a salt of the fatty acid. This method, using dibromo and chloropropanols and the sodium and potassium soaps, has been applied by Guth[2] with apparently great success. It was, therefore, tried in an attempt to prepare 2,3-distearin in quantity for another research. Exactly the conditions laid down by Guth were followed, namely, highly purified 2,3-dibromopropanol and sodium stearate were heated in sealed tubes in the ratio of one to a little more than two mols for seven hours at 140 to 150°. A mixture of substances was obtained, which could be recrystallized repeatedly from a hot, fairly concentrated solution of petroleum ether with practically no change in the melting point.[3] It was finally separated into three fractions and a residue. The fractions eventually proved to be stearic acid, distearin, and tristearin. A number of variations as to temperature and time of heating were tried. At temperatures sufficiently high to cause an appreciable reaction, there were always found considerable portions of stearic acid and some tristearin. At higher temperatures, 180 to 200°, large quantities of the latter substance were obtained. Under the best conditions, the method is very unsatisfactory, because, when any amount of diglyceride is obtained, tristearin is also formed. As the two substances are almost identical in solubility, the mixture is very difficult to separate to a satisfactory degree. In addition to the products indicated, there was also found in the most soluble portion, the residue, a substance containing bromine and stearic acid. This was not identified.

The most likely explanation for the presence of stearic acid seemed to be, of course, that the bromohydrin dissociates giving hydrobromic acid. An experiment proved that such was the case, and that at the temperature of a thymol bath, it breaks up completely into two molecules, and that one of them is hydrobromic acid. This dissociation is evident even at 100°, though very slight. From the facts indicated, it would appear that the following reactions occur:

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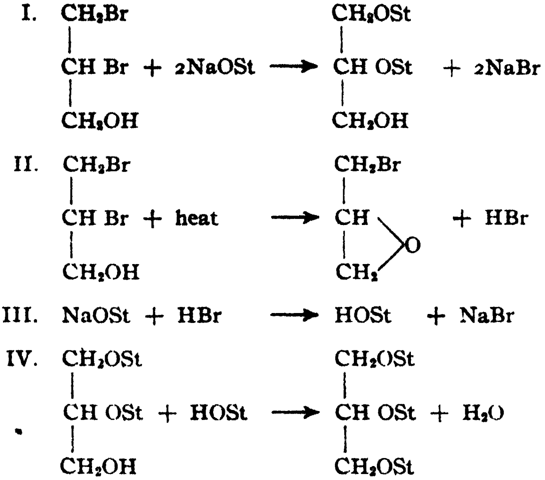
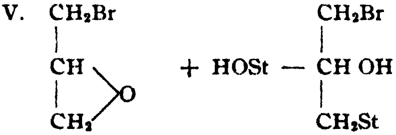
[1] *Loc. cit.*, cf. note 1, page 541 in the experimental part of this paper under the preparation of distearin.

[2] *Loc. cit.*

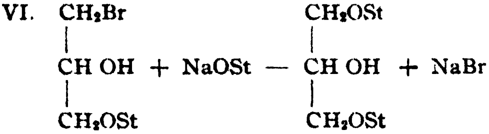
[3] Cf. Hundeshagen, *Loc. cit.*, p. 228.



Since such large quantities of the stearic acid were formed, it would seem likely that considerable amounts of epibromohydrin would also be present, and that it would act with the stearic acid as follows:



This reaction, or the action of only one molecule of stearic acid in I, would explain the presence of a substance containing bromine and stearic acid. One would then also expect the formation of some of the 1,3-isomer, as follows:



$$\text{VI.}\quad \begin{array}{l}CH_2Br\\ |\\ CH\,OH\\ |\\ CH_2OSt\end{array} + NaOSt - \begin{array}{l}CH_2OSt\\ |\\ CH\,OH\\ |\\ CH_2OSt\end{array} + NaBr$$

None of this substance was isolated, nor does the writer believe that more than traces of it were formed. It should be remembered, though, that in a mixture of compounds, resembling each other so closely in solubilities and melting points, it would be an exceedingly difficult matter to isolate it, if present only in small amounts.

The 2,3-diiodopropanol was prepared and tried. This is a comparatively unstable substance, and experiments showed that it is not at all serviceable for the object in mind.

Experiments with the lead soaps on the dibromide proved more successful, largely on account of the low melting point of the former, thus allowing the action to be carried out at lower temperatures. Nearly 20% of distearin could be obtained from these materials, fairly free from tristearin and hence comparatively easily purified. This proved to be the best procedure so far investigated.

3. By the action of salts of fatty acids on 2,3-dihalide propyl ammonium halide, with the subsequent elimination of the amino group with nitrous acid.

2,3-Dibromopropyl ammonium bromide was prepared, and was heated in solution and in a dry state with sufficient amount of the sodium or the lead soap to react with three bromine atoms. A charring occurred when these substances were heated alone. When heated in solution, a fair amount of decomposition took place, but relatively large quantities of stearic acid were formed, with only a small amount of an amino compound.

4. By the action of Twitchell's reagent on the 1-monochlorohydrin with the subsequent elimination of the halogen, and

5. By the action of the acid anhydrides on epihalide hydrins with the subsequent elimination of the halogen.

These methods were not investigated because the halogen in the distearyl halidehydrin seems to be very firmly bound. Grün and Theimer[1] write as follows concerning this: "Das Chlor [im distearyl chlorohydrin] erwies sich als so fest gebunden, dass es durch feuchtes Silberoxyd erst unter Bedingungen, bei denen gleichzeitig Esterverseifung erfolgt, eliminiert wird. Dementsprechend wurde auch, durch tagelanges Schütteln der benzolischen Lösung mit Silbercarbonat, Chlor nur spurenweise abgespalten."

They succeeded in getting partial elimination of the halogen, by heating the substance some hours with silver nitrite and a trace of acid in a current of hydrogen. The yield was not given, but it appears that the distearin required a number of recrystallizations for purification. These methods, therefore, do not seem to be as fruitful as the lead soap procedure.

Some new diglycerides have been prepared with collaborators, and their description will be the subject of a future communication.

Experimental Part.

Action of Sodium Stearate on 2,3-Dibromopropanol.—Highly purified stearic acid, having a neutralization value of 197 and melting at 69–70°, was used in all of this work. Samples of this were dissolved in absolute alcohol, and the solution poured into an alcoholic solution of sodium ethylate (from the calculated quantity of metallic sodium), the soap solution boiled, filtered, and the soap dried in a vacuum at 110°. The dibromopropanol was prepared and purified according to the method of Michael and Norton.[2]

Only a few typical examples of the many experiments will be given.

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[1] *Ber.*, **38**, 1794, 1907.

[2] *Z. Biol.*, **26**, 86.

1. Duplication of the experiments of Guth.[1] Twenty grams of the sodium stearate and 6.5 grams of the dibromopropanol were sealed in a glass tube and heated at 140–150° for seven hours, with frequent shaking, in an air bath. The product was extracted with boiling petroleum ether, and the extracted matter separating on cooling was recrystallized from the same solvent three times without appreciable change of melting point. The material was then dissolved in a large volume of ethyl ether, and the solution filtered before deposition was complete. Under the high power microscope, a few long needle crystals were observed, mixed with a considerable quantity of thin plates, and what appeared to be translucent amorphous material. The material was again dissolved in a large volume of ethyl ether, and an equal volume of petroleum ether added. After standing a short while, bunches of very fine needle crystals began to form. The rate of the crystallization increased rapidly and the form of the new crystals seemed to be different. It was later found that the material deposited in the latter part of the crystallization was composed largely of thin plates and ill-formed nodules. As there had been no intimation of a complex reaction taking place in this metathesis by the previous worker, the writer first supposed that the deposition of the crystals was too rapid for the building up of the needle form. Subsequently it was found that three distinct substances were present, and attempts were made to separate the needle crystals just before the other forms began to separate rapidly. Sometimes when the filtering was delayed too long, the disturbance of pouring the product on the filter would cause a very rapid separation of the non-needle formed substances. Even with the procedure indicated, it was found very difficult to separate the plates from the needles completely. In all, nineteen recrystallizations were made before a product was obtained completely free from plates. The substance crystallizes in spherical aggregates of long, thin needles, from ethyl ether and from petroleum ether, melting at 78.2° (corr.) and remelting within 30 minutes at the same temperature.[2]

Saponification number for distearin	179.8
Found.	183.0 and 181.0

Guth's compound crystallized in prismatic plates from petroleum ether and had a melting point of 74.5°. The product obtained by the writer is evidently 2,3-distearin, for Grün and Theimer have obtained[3] a distearin melting at 78.2° (corr.) by a method that leaves little doubt as to its constitution. They treated 1-monochloropropandiol with concentrated sulfuric acid and stearic acid, and isolated the chlorodistearin formed, and then by heating with silver nitrite and a trace of acid in a current of hydrogen procured the distearin.

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[1] *Loc. cit.*

[2] Hundeshagen (*J. prakt. Chem.*, 28, 228 (1883)), has minutely described the separation of a distearin which he obtained by action of stearic acid on glycerol His description so strikingly describes the product obtained by the writer that it is believed that Hundeshagen succeeded in getting the 2,3-isomer, although he found a melting point of 76.5°.

[3] *Ber.*, 40, 1995 (1907)

The samples of plates separated from the distearin were fractionally recrystallized. There was finally obtained a homogeneous product melting at 71.5° (corr.) and remelting at 55°. Equal quantities of these crystals and purified tristearin were dissolved in ether and the ether evaporated. The residue melted at 71.5° (corr.).

Saponification number for tristearin	189 1
Found	191.0 and 192 0

From the filtrates from the first crystallizations a considerable quantity of stearic acid, and a small quantity of a substance containing combined stearic acid and bromine was obtained.

2. Ten grams of soap and 3.5 grams of the dibromopropanol were heated at 180-200° for twelve hours, in a sealed tube, with occasional shaking, the melt extracted with a large quantity of ether,[1] and the residue of soap and sodium bromide separated by fractional solution in water. From the weight of the latter, (2.8+ grams) it was found that only 85% of the bromine was eliminated. The fatty portion yielded a large quantity of tristearin and smaller portions of distearin and stearic acid.

3. Forty-two grams of soap and 15 grams of the dibromopropanol were heated 72 hours at 130-135°. Due to an accident the sodium bromide was not weighed, but the greater portion of the soap was recovered unchanged, and the quantity of fat obtained was too small to make the utilization of this low temperature practicable. All three substances were formed, stearic acid, tri- and distearin, the relative proportion of the latter, however, was larger than when higher temperatures were used.

Many other variations of the experiments showed that the method was far from desirable. Probably the best procedure is to heat the materials for four hours at 150° with constant shaking, though even under these conditions the yield is small and the product is contaminated with much tristearin.

Dissociation of Dibromohydrin.—The dissociation of dibromohydrin at the temperature of the thymol bath was carried out by Dr. Heath of this laboratory as follows: Weighed samples of the freshly distilled dibromohydrin were dropped into a Victor Meyer molecular weight apparatus, and the gas collected over mercury. Previous experience had shown that concordant results could not be obtained by collecting it over water. The data afforded by this experiment showed that the dibromohydrin had been completely split up into two molecules. On opening the apparatus, very strong fumes of hydrobromic acid could be noted.

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[1] If a small volume of ether is used, material quantities of unchanged soap dissolve in the resulting concentrated solution of fat.

Experiments were made to determine if this dissociation occurred at lower temperatures. Hydrogen evolved from zinc and hydrochloric acid was passed through the following purification train: aqueous potassium hydroxide, concentrated sulfuric acid, solid potassium hydroxide, and phosphorus pentoxide. The gas from the phosphorus pentoxide tube was divided, and each portion passed through a tube containing 5 cc. of dibromohydrin immersed in ice-water, then through a condenser tube also immersed in ice-water, and into a tube containing a phenolphthalein solution made a distinct pink with sodium hydroxide. The gas was allowed to run for one hour in order to remove any free acid that the dibromohydrin might contain. The phenolphthalein was not appreciably decolorized, however. At the end of this period, one of the tubes containing the dibromohydrin was placed in boiling water. The pink phenolphthalein solution through which this portion of gas passed was practically decolorized within one hour, while the pink shade of the solution through which the other portion passed had not visibly changed. A similar experiment run at 150° gave very rapid decolorization of the phenolphthalein solution. It seems clear, then, that even at 100°, very slight quantities of hydrobromic acid are evolved from the dibromohydrin.

Dibromohydrin itself reacts acid. If a small quantity of it is added to water containing slightly pink phenolphthalein, the latter is rapidly decolorized, and one may, from time to time, add portions of sodium hydroxide to pink, and the color will in each case disappear. To litmus, the material gives only a faint acid tint immediately, but on standing a short while, a very pronounced red color appears.

The extent of dissociation in aqueous solutions of dibromohydrin will be investigated.

Experiment with 2,3-Diiodopropanol.—This substance was tried instead of the corresponding bromine derivative in the hope that the decomposition could be brought about at lower temperatures and thus prevent the formation of any amount of the tristearin. It was prepared as follows: 25 grams of iodine and 10 grams of allyl alcohol were stirred in a beaker for some time. A considerable heat was evolved, and after about an hour, the contents solidified. The cake was pressed out on a porous tile, mashed up in a mortar with dilute solution of sodium hydroxide until perfectly white, washed with water, sucked dry on a filter, and finally washed with petroleum ether. The product was obtained as beautiful, long, silky needles, by the slow addition of petroleum ether to its solution in carbon disulfide. It is markedly unstable, undergoing spontaneous decomposition at ordinary temperatures. An extra fine sample of these needle crystals, in a glass-stoppered amber bottle, was placed in a dark cupboard.

After three weeks the bottle contained a dark, thick liquid and some crystals of iodine.

The action of silver stearate on this iodide in aqueous alcohol at slightly elevated temperatures was not fruitful. A solution of the diiodide in benzene was dropped very slowly into a boiling solution of sodium stearate in amyl alcohol. Nothing of a fatty nature but stearic acid was isolated from the reaction flask. Similar results were obtained when xylene was substituted for the amyl alcohol and the benzene. On fusing with soap, hydriodic acid and iodine were eliminated.

Action of Lead Stearate on 2,3-Dibromopropanol.—Lead stearate (20 grams) and dibromopropanol (5.5 grams) were heated in a pressure bottle four hours with constant shaking in an air bath at 122°. The melt was extracted with ether, filtered, alcohol added and the solution titrated with sodium hydroxide solution to neutrality to phenolphthalein. 12.20 cc. of the solution containing 0.0354 gram of sodium hydroxide per cc. were needed, indicating the presence of about 3.0 grams of stearic acid. Four grams of fat were separated from the soap. This was not pure distearin, however, and several recrystallizations were needed to purify it. If all the stearate had been converted into distearin, 16 grams would have been obtained. It is likely, then, that the yield is nearly 20%, though that amount can not be conveniently isolated, as its separation from tristearin can never be made sharp.

Experiments at higher temperatures yielded more distearin, but the difficulty of eliminating the increased quantity of tristearin more than offset the advantage.

Action of Lead and Sodium Soaps on 2,3-Dibromopropylammonium bromide.—This bromide was prepared for the writer by Mr. R. R. Stevens as follows: The allyl amine was obtained from allyl isothiocyanate by boiling the latter with 20% aqueous hydrochloric acid according to Gabriel and Eschenbach.[1] The calculated quantity of hydrobromic acid was added to the amine and the resulting hydrobromide converted into 2,3-dibromopropylammonium bromide by the direct addition of bromine. This substance melted at 170.2° (corr.).

Fusion with lead stearate was not fruitful. This substance seemed to act catalytically on the carbonization of the amino compound.

Four and one-half grams of dibromopropylammonium bromide were dissolved in 50 cc. of propyl alcohol, toluene poured in until the amine started to precipitate (150 cc.), and 15 grams of sodium stearate added. After boiling 25 hours, the solution was decanted from the precipitated salt, evaporated under diminished pressure, and the residue dissolved in alcohol and ether, and alcoholic potassium hydroxide added to neutrality. Acidity, calculated to stearic acid, indicated that 7.9 grams of that substance were present. The soap was filtered off, the filtrate evaporated and the residue purified by a number of recrystallizations from absolute ether and from aqueous alcohol. There was thus obtained a few tenths of a gram of a substance which separated from alcohol as a voluminous precipitate resembling precipitated aluminum hydroxide. It gave a strong qualitative test for nitrogen and a rather weak one for bromine, but its ether solution did not yield a precipitate with alcoholic platinic chloride or with hydrogen chloride. Neither did its alcoholic solution give a precipitate with alcoholic silver nitrate. A Dumas nitrogen determination on a small sample gave 2.64% nitrogen. Another small sample (m. 88–90°, uncorr.) prepared in a similar manner, gave 2.69% nitrogen. The amino diglyceride would give 2.25% nitrogen. It is possible that the products obtained were mixtures, though no evidence for that fact could be obtained by use of the microscope or from the change of character on recrystallization. The analyses agree with the theoretical values for stearylbromoglyceryl-dipropyl amine, but the formation of this does not seem likely.

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[1] *Ber.*, 30, 1124 (1897).

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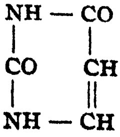
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON PYRIMIDINES. LXVIII. THE STRUCTURE OF RITTHAUSEN'S DIVICINE.

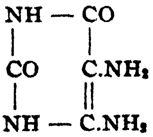
BY TREAT B JOHNSON AND CARL O. JOHNS.

Received January 9, 1914

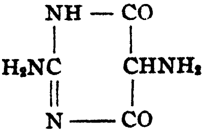
In a recent publication[1] from this laboratory were recorded some new speculations regarding the origin of purines in plants. Attention was called to the most interesting fact that the nitrogenous substance *divicine*, which Ritthausen[2] obtained from *vicine* of vetch seeds by hydrolysis with sulfuric acid, may be a pyrimidine compound. In fact, the formula $C_4H_7O_2N_4$, which was assigned to the base by Ritthausen, differs from that of a diamino-derivative of uracil (II), or its isomer 2,5-diamino-4,6-dioxypyrimidine (III) by only one hydrogen atom. The low percentage of hydrogen, and the significant carbon and nitrogen ratio of 1 : 1, exclude the possibility of the base being an acyclic compound. Since pyrimidines of this type have never been observed to occur in nature, it



(Uracil) (I)



(II)



(III)

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[1] Johnson, THIS JOURNAL, 36, 337.

[2] For literature references see paper by Johnson, *Loc cit.*

was, therefore, of the greatest importance, from a biochemical standpoint, to compare critically the properties of these two pyrimidine bases with those of Ritthausen's divicine.[1] This has now been done, and the description of the interesting relationships, which the work has revealed, forms the subject of this paper.

We wish to call attention first to the analytical results obtained by Ritthausen, which are recorded in this investigator's last paper on divicine.[2] These, together with the theoretical values for carbon, hydrogen and nitrogen in divicine and 4,5-diaminouracil are recorded in Table I, below.

TABLE I.

	Calculated for $C_4H_7O_2N_4$.		Calculated for $C_4H_6O_2N_4$.
C	33.5	C	33.8
H	4.8	H	4.22
N	39.16	N	39.4

VALUES OBTAINED BY RITTHAUSEN.

Percentage of C.	Percentage of H.	Percentage of N.
32 91	4.88	38.82
33.32	4 59	38.77
33.88	4.89	38.95
33.83	4.47	38.92
33.56	4.84	38.23
34.04	4.62	38.88
33.41	4.59	...
33.69	4.74	...
34.4	4.34	...
33.89	4.50	...
33.80	..	..

While the analytical data are of interest, on the other hand, it is apparent from inspection that one cannot safely conclude, from the results, whether divicine is to be represented by formula $C_4H_7O_2N_4$ or $C_4H_6O_2N_4$.[3] The high percentage of nitrogen and the carbon and nitrogen ratios of 1 : 1 afford evidence of a pyrimidine compound. The substance is evidently not ethylene diurea[4] (glycouril, IV) and its stability, in the presence of alkali, excludes the possibility of its being a hydantoin derivative containing an acid amide grouping as represented by formulas V, and VI.

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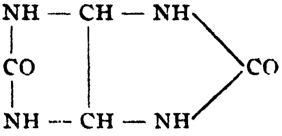
[1] It is of especial interest to note here that Kutscher (*Z. physiol. Chem.*, **38**, 176 (1903)) believed he obtained an oxydiaminopyrimidine from yeast nucleic acid, by decomposing this acid at a high temperature with sulfuric acid. This observation has previously received attention from this laboratory and Johnson and Johns (*Amer. Chem. J.*, **34**, 554) actually found that 2,5-diamino-6-oxypyrimidine agreed in its chemical behavior, so far as they were able to judge from comparative tests, with Kutscher's unknown base.

[2] *J. prakt. Chem.*, **59**, 482 (1899).

[3] It is important to call attention here to the fact, that this formula of Ritthausen's $C_4H_7O_2N_4$ is impossible unless it be doubled, because it does not conform to the principle that the number of atoms of odd valence in a carbon compound must be an even number.

[4] *Ber.*, **19**, 2477.



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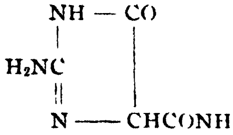
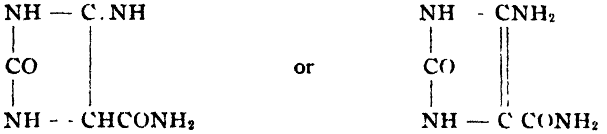


(V)



(VI)

Ritthausen has also summarized, in his last paper on divicine,[1] further results of his work on this base and gives a series of precipitation and color reactions which are characteristic of divicine. These tests are recorded verbatim in Table II, below. Some of these tests are unique and undoubtedly specific for certain types of compounds.

We have now applied all these tests of Ritthausen's with both the 2,5-diamino- and the 4,5-diaminopyrimidines (III) and (II), respectively, and have made the interesting observation that 4,5-diaminouracil (II) responds positively to every one. In fact, the agreement in chemical behavior is so perfect, that one would actually be justified in concluding that this pyrimidine and divicine are identical. On the other hand, as will be observed by inspection of Table II, the isomeric 2,5-diamino-4,6-dioxypyrimidine (II), failed to respond to all of Ritthausen's tests. This base is also far less soluble in water than divicine. Furthermore, it is so susceptible to oxidation that it is practically impossible to isolate it in a pure condition. It is of interest to note, in this connection, that both of these pyrimidines were isolated by Traube[2] in the form of their stable sulfates. He writes as follows regarding the 2,5-diaminopyrimidine (III): "Der Amidokörper bildet einen gelblichen, pulverigen, in Wasser kaum löslichen Niederschlag, der sich in feuchtem Zustande an der Luft rasch dunkelroth färbt."

The three most characteristic tests of the ten applied by Ritthausen with divicine (Table II) are 1, 3 and 4. The reduction of silver salts to metallic silver is a characteristic behavior, which is in accord with previous observations, and is a very strong argument, from a chemical standpoint, that Ritthausen was dealing with an orthodiamine $H_2N\overset{|}{C} = \overset{|}{C}NH_2$. The observation that both of our pyrimidine bases give the same

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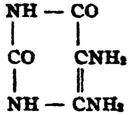
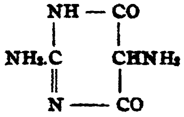
[1] *Loc. cit.*

[2] *Ber.*, 26, 2556; 33, 1382

TABLE II.

Ritthausen's Description of Divicine,[1]	Behavior of 2,6 - Dioxy - 4,5 - diaminopyrimidine,	Behavior of 4,6 - Dioxy - 2,5 - diaminopyrimidine,
$C_4H_7O_2N_4$(?).	 or $C_4H_6O_2N_4$	 or $C_4H_6O_2N_4$.
1. Ag—Lösung—wird sofort zu Ag reducirt.	1. Immediate reduction with deposition of silver on adding silver nitrate to an aqueous solution of the pyrimidine.	1. Silver nitrate reduced to metallic silver when added to an aqueous solution of the pyrimidine.
2. $HgCl_2$—giebt augenblicklich HgCl.	2. $HgCl_2$ produces a precipitate, which changes to a white powder on heating.	2. Mercuric chloride gave a flaky precipitate which collected together on heating.
3. Phosphor-Molybdänsäure—wird sofort tiefblau.	3. Phosphomolybdic acid produced at once a deep blue color.	3. Phosphomolybdic acid produced at once a deep blue color.
4. Phosphor-Wolframsäure — sofort schmutzig graublauer Niederschlag bei Zusatz verdünnter Schwefelsäure.	4. The addition of phosphotungstic acid produced a grayish yellow precipitate.	4. Phosphotungstic acid gave a characteristic blue color, but no precipitate.
5. Pikrinsäure—reichlicher Niederschlag, gelblich flockig.	5. Picric acid gave a yellow precipitate on standing.	5. Picric acid gave no precipitate.
6. Kalium-Wismuthjodid—nach längerer Zeit Niederschlag in der Kälte, erwärmt—sofortige rothbraune Fällung.	6. Potassium-bismuthiodide reacted giving a heavy yellow precipitate.	6. No precipitate on addition of potassium-bismuth iodide solution.
7. Kalium - Quecksilberjodid — nach längerer Zeit schmutziggrauer Niederschlag.	7. No apparent reaction. On standing a yellowish precipitate finally deposited.	7. No apparent reaction. On standing a yellowish precipitate finally deposited.
8. Platinchlorid—wird entfärbt, ohne Niederschlag zu erzeugen.	8. Chloroplatinic acid gave no precipitate.	8. Chloroplatinic acid gave no precipitate
9. Beim Kochen mit Kalilauge oder Natriumcarbonat wird die Lösung fortdauernd dunkler, endlich rothbraun.	9. On boiling with an aqueous solution of potassium hydroxide an orange color was produced without evolution of ammonia.	9. On boiling with an aqueous solution of potassium hydroxide a violet color is first produced, but finally changes to red on continued heating
10. Durch Salpetersäure wird die Lösung getrübt und es scheidet sich bald ein krystallinischer Niederschlag ab.	10. When nitric acid was added to a strong, aqueous solution of the pyrimidine a turbidity resulted and finally a crystalline precipitate deposited	10. No precipitate was obtained on adding nitric acid to an aqueous solution of the pyrimidine

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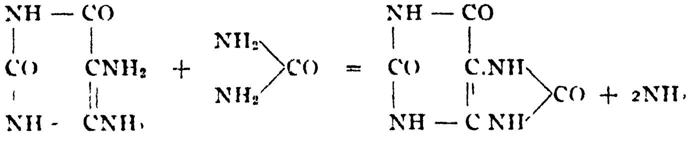
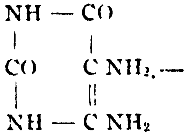
[1] *J. prakt Chem.*, **59**, 484.

characteristic blue solutions as Ritthausen's divicine, when combined in aqueous solution with phosphomolybdic acid, is especially significant, because both of the pyrimidines (II), and (III) contain an amino group in the 5-position of the pyrimidine ring. This observation and those of our former co-workers Lewis and Nicolet[1] have aroused a new interest in the practical utility of these acids as color reagents[2] for certain types of organic compounds. That the 5-amino group functionates in these pyrimidine reactions is supported by further evidence which will be discussed in a future paper from this laboratory. It appears probable, therefore, from a consideration of the experimental evidence, that Ritthausen's *divicine* is identical with 4,5-diaminouracil (II). There remained to be developed, however, a reliable test by which such a constitution could be easily established. We are now able to state that this can easily be accomplished by heating divicine with urea. We find that 4,5-diaminouracil (II) is converted quantitatively into uric acid (VII) when heated with urea at 170-180°. The interaction of divicine with urea with formation of this purine (VII) would establish beyond doubt the structure of the base.


(II) (VII)

Experimental Part.

2,6-Dioxy-4,5-diaminopyrimidine (4,5-Diaminouracil),



This pyrimidine was prepared from its sulfate, which was synthesized according to the directions of Traube.[3] The salt was finely pulverized and then mixed with just enough water to make a thin paste. The sulfuric acid was then exactly neutralized by triturating the paste with the required amount of normal sodium hydroxide solution. The free pyrimidine was obtained as a light gray powder. This was separated by filtration, washed with water to remove sodium sulfate and finally with alcohol and ether. The pyrimidine was then dried at 75° and used for our experiments without further purification. An attempt to purify the base by crystallization from water was not successful because the pyrimidine undergoes partial decomposition when warmed with water and separates in an amorphous condition. When sulfuric acid is added to an aqueous solution of the base the corresponding sulfate separates immediately.

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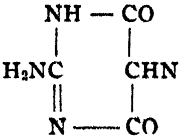
[1] *J. Biol. Chem.*, **16**, 369.

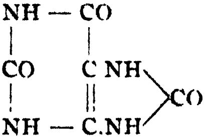
[2] Folin and Macallum, *J. Biol. Chem.*, **11**, 265; Folin and Denis, *Ibid.*, **12**, 239; **14**, 95.

[3] *Loc. cit.*



$$\begin{array}{lcl} \mathrm{NH} & - & \mathrm{CO} \\ | & & | \\ \mathrm{H_2NC} & & \mathrm{CHNH_2} \\ \| & & | \\ \mathrm{N} & - & \mathrm{CO} \end{array}$$

4,6-Dioxy-2,5-diaminopyrimidine, —The sulfate of 4,6-dioxy-2,5-diaminopyrimidine was prepared according to Traube's[1] directions by dissolving the ammonium salt of 2-amino-4,6-dioxy-5-isonitrosopyrimidine in dilute sulfuric acid and then saturating the solution (while warm) with hydrogen sulfide. This treatment was continued until the reduction was complete. The crude sulfate was then separated by filtration and washed with water and alcohol. The free sulfur which was present was then removed by washing with carbon disulfide and the salt finally washed with ether and dried at 75°. The free pyrimidine base was then liberated according to the same procedure as applied in the case of the 4,5-diaminopyrimidine. The pyrimidine was washed in turn with water, alcohol and ether and then dried at 75°. This base is much more unstable than the isomeric 4,5-diaminopyrimidine and if exposed to the air, while moist, it rapidly undergoes oxidation becoming purple. Its aqueous solution rapidly becomes colored, finally assuming a brilliant potassium permanganate color.



$$\begin{array}{lcll} \mathrm{NH} & - & \mathrm{CO} & \\ | & & | & \\ \mathrm{CO} & & \mathrm{C\,NH} & \\ | & & \| & \rangle\mathrm{CO} \\ \mathrm{NH} & - & \mathrm{C.NH} & \end{array}$$

The Conversion of 2,6-Dioxy-4,5-diaminopyrimidine into 2,6,8-Trioxypurine or Uric Acid, —One gram of 2,6-dioxy-4,5-diaminopyrimidine and 1 gram of urea were pulverized together and the dry mixture then heated in an oil bath at 170-180° for one hour. The brown residue which was obtained was then dissolved in hot, dilute sodium hydroxide solution and the solution filtered. On acidifying with dilute hydrochloric acid there was an immediate precipitation of uric acid. This was washed with water and alcohol and dried at 120°. The weight was 1 gram. The formation of the purine is so smooth that extremely small quantities of the pyrimidine can be identified in this manner.

Calculated for $C_5H_4O_3N_4$: N, 33.33%; found: N, 33.19%.

NEW HAVEN, CONN.

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[1] *Loc. cit.*

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

ON THE ACTION OF SODIUM HYDROXIDE ON IODOANIL.[1]

BY C LORING JACKSON AND E K. BOLTON.

Received January 19, 1914

A study of the literature has shown that, when chloroanil or bromoanil is treated with an alkaline hydroxide, the product is chloroanilic acid, or bromoanilic acid[2] with a single exception observed by Kehrmann,[3] who, while obtaining chloroanilic acid with alcoholic potassium hydroxide in the cold, found that when hot the product was metadiethoxydichloroquinone. Experiments of our own also with bromoanil led in every case to bromoanilic acid; but Torrey and Hunter[4] observed that, when iodoanil was treated with alkalies, the product frequently was not iodoanilic acid; and this difference in the behavior of chloroanil and bromoanil, on the one hand, and iodoanil, on the other, is so interesting that we have studied it in detail in our continuation of their work.

The products obtained by the action of alkalies on iodoanil differ according to the conditions of the reaction. By the action of sodium hydroxide on iodoanil, suspended in a mixture of 30 cc. of water and 15 cc. of alcohol, a sodium salt is formed, which looks like sodium iodoanilate, and, like it, crystallizes with water in dark purple prisms terminated at each end by two planes at an obtuse angle, leaving, however, when dried a purplish black residue instead of the brownish purple anhydrous sodium iodoanilate. On acidification a substance is precipitated, which crystallizes from hot toluene in red needles, in the cold in rhombic plates containing toluene of crystallization. This might be a description of iodoanilic acid, and, although a careful comparison reveals slight differences, such as a tendency to spindle forms in the needles, and truncation of the obtuse angles of the plates, neither of which appear in iodoanilic acid, these are rather differences in habit, such as might be caused by the presence of an impurity, than real differences in crystalline form. In view of these marked similarities very convincing arguments are necessary to show that we have a new substance and not somewhat impure iodoanilic acid, especially as most various reagents convert it into iodoanilic acid or some of its derivatives.

Our reasons for believing it to be a new compound are the following: (1) The new product contains about one and a half per cent. more iodine than iodoanilic acid, and, as six agreeing analyses were obtained from six different preparations crystallized from one to four times from toluene, it can hardly be that the excess of iodine was due to an impurity. (2) We next tested for an impurity, and, as this must raise the percentage of iodine, the only probable ones were sodium iodide and iodoanil. A specimen of our salt, therefore, was decomposed with enough dilute sulfuric acid to precipitate most of the organic matter, and the filtrate tested for an iodide, when it gave a trace of a red precipitate (probably only silver iodoanilate) but, even if it were in part silver iodide, the amount was very far from enough to account for the difference in the percentages. As the precipitate with sulfuric acid dissolved completely in water, no iodoanil could be present. This solution was then boiled for a few minutes, which converts the substance completely into iodoanilic acid, and after precipitating this with an excess of dilute sulfuric acid the test for iodide was repeated with the same negative result as before. No sodium iodide or iodoanil, therefore, was present.

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Elmer Keiser Bolton.

[2] Stenhouse, *J. Chem. Soc.*, 8, 6 (1870); Graebe, *Ann.*, 263, 16 (1891).

[3] *J. prakt. Chem.*, 39, 318 (1889).

[4] THIS JOURNAL, 34, 702 (1912).

(3) This last experiment seems to us to give a conclusive proof of the nature of the compound, for starting with a substance containing 66.50% of iodine we have converted it by boiling with water into iodoanilic acid, which contains only 64.78%, and this lowering of the amount of iodine has been accompanied by no setting free of any compound containing iodine. The only explanation we can find for these observations is that the substance is the hemiether of iodoanilic acid, I, $[C_6I_2(OH)O_2]_2O$, and by taking up one molecule of water it is converted into iodoanilic acid with its smaller percentage of iodine. Such a hemiether might well show a marked resemblance to the acid with only slight differences as described above, and would undergo the change to the acid with a great variety of reagents.

(4) The salt to be expected from the hemiether $[C_6I_2(ONa)O_2]_2O$ would contain 5.68% of sodium, the sodium iodoanilate 10.55%, so that it seemed analyses of this sodium salt would settle the question. The material used for analysis was made direct from iodoanil and sodium hydroxide, and on acidification gave our hemiether. The results of 3 analyses agreed with those for sodium iodoanilate as nearly as could be expected from a substance so unstable that we could purify it only by washing with alcohol, but in spite of this it cannot be sodium iodoanilate, as determinations of the water of crystallization showed that our salt contained 9.95, 9.96%, the iodoanilate 20.12, 20.25%, so that, although the sodium determinations tell against the hemiether hypothesis, the amounts of water furnish us another strong argument in favor of it. To reconcile the two we feel obliged to assign to the salt the somewhat improbable formula, II, $[C_6I_2(ONa)O(OHONa)]_2O$, in which one molecule of sodium hydroxide has been added to one of the quinone oxygens; and we do this in face of a serious objection based

on the color of the salt, which as a hemiacetal ought to be lighter than the free acid, whereas it is darker—purple instead of red.

(5) The hemiether begins to decompose at 215° (uncorr.), iodoanilic acid at 205° (uncorr.); but if our substance were impure iodoanilic acid, it would melt below, not above, the pure substance. The five arguments just given seem to us to prove that our compound is the hemiether of iodoanilic acid.

The hemiether passes with great ease into iodoanilic acid, or its derivatives; water, or sodium hydroxide, gives two molecules of the acid; acetic anhydride diiododiacetoxyquinone; aniline, dianilinoquinone by saponification of the hemiether followed by replacement of the hydroxyls by aniline radicals and the atoms of iodine by hydrogen (two interesting exhibitions of the loosening effect of quinone oxygen).

When the sodium hydroxide acting on the iodoanil was dissolved in 50 parts of alcohol to 10 of water, a different result was obtained from that given by the previous experiments with 15 of alcohol and 30 of water, for, on adding an acid, a product was precipitated, which decomposed between 160° and 180°, and contained the ethoxy group. In our opinion this is diiodohydroxyethoxyquinone (monoethylether of iodoanilic acid), III, $C_6I_2(OH)(OC_2H_5)O_2$, although the formula, IV, $[C_6I_2(OC_2H_5)O_2]_2O$, must also be considered, according to which it is the ethyl ether of the hemiether formed when less alcohol is present. Most of our observations agree equally well, or rather equally badly with either of these formulas, showing, however, a slight preference for III, but there is one which seems to us to pronounce distinctly in favor of III, so we have adopted it, although we cannot claim that it rests on a very secure foundation. This single observation, that we cannot bring into harmony with IV, is the formation of what seems to be diiododiethoxyquinone, $C_6I_2(OC_2H_5)_2O_2$, by the action of ethyl bromide on the silver, or potassium, salt of our substance. The observations telling in favor of III but not excluding IV are the following: Although the percentages of iodine for the two formulas differ by 1.3%, we could not decide between them in this way, as our results covered the whole interval. The specimens most frequently crystallized, however, and, therefore the purest, came nearest to III; and yet, if IV were correct, this could be explained on the supposition that the hemiether was slowly converted into the hydroxyl compound by the water in the solvent—$[C_6I_2(C_2H_5O)O_2]_2O$ to $C_6I_2(C_2H_5O)(HO)O_2$—as observed with the hydroxyhemiether; but such a reaction should be accompanied by a change in properties, and, as none was observed, its occurrence is very doubtful, so that the best explanation of the phenomena is that the change in composition was due to purification and that III is the true formula. This view is supported by the fact that analyses of the silver salt and of the free substance prepared from the hemiacetal gave results agreeing with III, since both these products should be especially pure.

The most striking derivative of our compound was a bluish black potassium salt, which was stable enough to be crystallized from alcohol, and could be prepared by the action of potassium hydroxide on the free acid or on iodoanil itself. The analyses of this salt gave results nearly 2% too low for the amount of iodine in $C_6I_2(OC_2H_5)(OK)O_2$, and in order to make them agree with III it is necessary to assume one molecule of water in the salt, which seems improbable, since it was dried at 100°. Unfortunately we could not test this assumption by experiment, as the substance began to decompose at higher temperatures. On the other hand the percentages found agree with those calculated for the salt of IV, $[C_6I_2(OC_2H_5)(OHOK)O_2]_2O$. This formula is certainly a strange one, yet it will be remembered that we were driven to adopt a similar one in studying the hydroxyhemiether, although such a salt, being related to the hemiacetals, should be lighter in color than the quinone, and in both cases it was darker, here black from an orange-red quinone. On the other hand, with III we should expect a darker salt from the frequent auxochrome effect of salt formation. Again, if a hemiacetal, the salt should have but a slight stability, whereas it can be crystallized from alcohol without decomposition. Of the two rather doubtful hypotheses, therefore, it seems to us the presence of water required by III is the more probable.

Aniline acting on the free substance converts it easily into the salt $C_6I_2(C_6H_5NH)(OHNH_2C_6H_5)O_2$, which gives with acids the dark blue diiodoanilinohydroxyquinone, $C_6I_2(C_6H_5NH)(OH)O_2$, whereas potassium hydroxide gives the salt of the unaltered substance. If IV is correct, the feeble aniline must then have split the hemiether to form the aniline salt of the substituted quinone, while the stronger potassium hydroxide has produced no such decomposition. With III no such anomalous assumption is needed, since both aniline and potassium hydroxide simply convert the substances into the corresponding salts.

Acetyl chloride converts the potassium salt into the free acid instead of an acetyl compound, which perhaps agrees better with IV than with III, especially as a similar observation was made with the hydroxyhemiether, but, as this is the only case in which IV is to be preferred, we think that the discussion just given justifies our adoption of III.

The formation of this diiodohydroxyethoxyquinone is not out of harmony with the appearance of the hemiether of iodoanilic acid in the experiments with less alcohol, as each reaction consists in the formation of an ether, the iodine compound reacting with the sodium salt present —$C_6I_2(ONa)_2O_2$ when water is the principal solvent, but with alcohol $NaOC_2H_5$.

It is a curious fact that, whereas the potassium salt $C_6I_2(OC_2H_5)(OK)O_2$ is obtained easily from either the free acid or from iodoanil, the same method with sodium hydroxide converted the free acid into sodium iodoanilate, and with iodoanil produced an unmanageable solution, from which there was little chance of isolating an unstable salt. This striking difference between the behavior of sodium and potassium hydroxides is undoubtedly explained by the slight solubility of the potassium salt, which removed it at once out of the reach of further action, whereas the sodium salt was found to be freely soluble, when at last we succeeded in making it by the action of sodium chloride on the silver salt.

In the action of sodium or potassium hydroxide on iodoanil the product was sometimes the salt, sometimes the iodoanilate, and at others diiododiethoxyquinone, which was the invariable product, when alcohol was the only solvent, while with methyl alcohol the reaction went further, giving the salt of the hemiacetal of diiododimethoxyquinone. It will be interesting to determine whether this greater tendency toward the formation of the methyl than the ethyl hemiacetal appears in other cases.

In general, then, our work has brought out two peculiarities in the behavior of iodoanil with alkaline hydroxides, a tendency toward the replacement of two of its para halogen atoms by different radicals, of which we can find no case with chloroanil or bromoanil, and a tendency toward the replacement of halogen by the ethoxy radical, of which only one case[1] with chloroanil has been recorded, or toward the analogous formation of the hemiether. Too much weight should not be put upon these negative results, however, until a more extended study of chloroanil and bromoanil has been made. We have found only one explanation for these differences in effect between iodine and the other halogens, which we give for what it may be worth. According to this the sodium ethylate in the alcoholic sodium hydroxide first forms a diethoxydihalogenquinone, which is afterward saponified more or less completely by the sodium hydroxide. The amount of saponification will depend on the loosening effect of the negative radicals present upon the ethyl groups, and, if the slightly negative iodine is present, after one of the C_2H_5O groups has been converted into NaO, the presence of the sodium in the molecule may well neutralize completely the loosening effect of the iodine, halting the reaction at the diiodohydroxyethoxyquinone, whereas with the much more negative chlorine, or bromine, the sodium would be unable to overcome the loosening effect, so that both ethoxy groups would be saponified.

Our experiments with aniline have thrown some light on the comparative reactivity of different radicals in these substituted quinones. The hydroxy group assists the replacement of an ethoxy group in the para position, $C_6I_2(C_2H_5O)(HO)O_2$ gave $C_6I_2(C_6H_5NH)(HO)O_2$, but an ethoxy group produces no such effect on a second in the para position, aniline showing no action with $C_6I_2(C_2H_5O)_2O_2$. The acetoxy group is more easily replaced than the hydroxy or ethoxy group, as $C_6I_2(C_2H_5O)(C_2H_3O_2)O_2$ gave in the cold $C_6I_2(C_2H_5O)(C_6H_5NH)O_2$; and, since it gives, when hot, $C_6I_2(C_6H_5NH)_2O_2$, it seems as if the anilino group must loosen the ethoxy group.

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[1] Kehrmann, *J. prakt. Chem*., 39, 318 (1889)

The retention of iodine in the ring, when aniline converts the diiodoethoxyacetoxyquinone into diiododianilinoquinone is certainly strange, because the diiodoanilinoacetoxyquinone and the hemiether of iodoanilic acid both give dianilinoquinone (free from iodine), when treated with aniline.

A study of the colors of these compounds shows that in the quinones with oxygen radicals the salts are more deeply colored than the free quinones; $[C_6I_2(OH)O_2]_2O$ and $C_6I_2(C_2H_5O)(OH)O_2$ are red, their salts black. With a nitrogen radical exactly the reverse is the case, the quinone being more deeply colored than the salt; $C_6I_2(C_6H_5NH)(OH)O_2$ is navy blue, the salts red. This seems to be a rule of general application with paraquinones containing halogens, since the three halogen anilic acids are lighter colored than their salts, while the chloro-[1] or bromoanilamic[2] acid is black, its ammonium salt brown.

In these compounds also the color is deeper, when the two para positions are occupied by different radicals, than when they carry two radicals of the same sort.

Different radicals.	The same radical.
$C_6I_2(C_2H_5O)(OH)O_2$, red	$C_6I_2(C_2H_5O)_2O_2$, orange-red
$C_6I_2(C_2H_5O)(OC_2H_3O)O_2$, red	$C_6I_2(OC_2H_3O)_2O_2$, yellow
$C_6I_2(C_2H_5O)(C_6H_5NH)O_2$, blue	$C_6I_2(C_6H_5NH)_2O_2$, brown
$C_6I_2(OH)(C_6H_5NH)O_2$, black	$C_6I_2(OH)_2O_2$ orange-red

We have been able to find only two well marked cases of this kind in the literature. $C_6Br_2(OH)(NH_2)O_2$ is almost black, while $C_6Br_2(NH_2)_2O_2$ is brownish red and bromoanilic acid reddish. $C_6H_2(OH)(C_6H_5NH)O_2$ is blue, $C_6H_2(C_6H_5NH)_2O_2$ reddish brown and $C_6H_2(OH)_2O_2$ dark yellow.

Experimental.

Action of Sodium Hydroxide on Iodoanil.—The product obtained differs with the amount of alcohol present. We shall begin our account of these reactions with the case, where the quantity of alcohol is small.

The Hemiether of Iodoanilic acid, $[C_6I_2(OH)O_2]_2O$.—Ten grams of iodoanil,[3] suspended in a mixture of 15 cc. of alcohol and 30 cc. of water, were treated with 15 cc. of a 50% aqueous solution of sodium hydroxide. A reaction accompanied with evolution of heat took place at once, forming a deep brownish red solution and giving off a disagreeable penetrating smell. The addition of dilute sulfuric acid at this point threw down an orange-red precipitate of the hemiether, which was washed with water, until a purple color in the filtrate showed that the substance was beginning to dissolve, after which it was crystallized twice from toluene (Analysis I). A better way of preparing the substance consisted in shaking the solution of the iodoanil in the sodium hydroxide for several minutes, when the sodium salt of the hemiether began to crystallize, and, after the deposition was complete, it was filtered out, washed with alcohol (in which it was practically insoluble) and then dissolved in a small quantity of water, acidified with dilute sulfuric acid, and purified as described above. The substance was dried at 100°; II, III, IV.

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[1] Erdmann, *Ann.*, 48, 321.

[2] Stenhouse, *Ibid.*, 91, 313.

[3] Prepared as described in THIS JOURNAL, 36, 305 (1914).

Subst., I, 0.2066; II, 0.2124; III, 0.2338, IV, 0.2312. AgI, 0.2550, 0.2616, 0.2896, 0.2835.

Calculated $[C_6I_2(OH)O_2]_2O$· I, 66.30 $C_6I_2(OH)_2O_2$, I, 64.78

Found. I, I, 66.72; II, 66.58; III, 66.96; IV. 66.28

Attempts to determine the amount of toluene of crystallization gave no results worth recording, because it was held so loosely that it was impossible to dry the crystals with certainty. It seemed to amount to 3 or more molecules.

To determine whether the high percentages of iodine obtained were due to a new compound (the hemiether), or to iodoanilic acid containing an impurity richer in iodine the following tests were made with a specimen of the substance. The only probable impurities of this sort are iodoanil and sodium iodide. To test for sodium iodide the substance was treated with 25 cc. of water in the cold, after which the undissolved portion was filtered out, and what had dissolved precipitated by the addition of nitric acid. Silver nitrate then gave only an insignificant precipitate, which was evidently silver iodoanilate from its red color. As the presence of over 5% of sodium iodide would be necessary to raise the percentage of iodine from 64.78 in iodoanilic acid to the 66.50% found, it is evident that the cause of the high percentage of iodine is not sodium iodide. The residue from this treatment with water was then dissolved in more water, and upon filtration no insoluble residue was obtained, showing the absence of iodoanil. To detect any sodium iodide, which might have escaped the first test by imprisonment in the crystals, the complete solution was boiled until the substance had been converted into iodoanilic acid, which was then precipitated by acidification, and the filtrate treated with silver nitrate, giving, as before, nothing but a very slight red precipitate of silver iodoanilate. Our substance, therefore, was free from an impurity of sodium iodide or iodoanil.

Properties of the Hemiether of Iodoanilic Acid.—It crystallizes from warm toluene in red needles, often spindle-shaped, which we believe to be free from toluene of crystallization; but the crystals deposited, after the solution has grown cool, differ from these, as they are orange-red, diamond-shaped plates with the obtuse angles truncated, and contain toluene of crystallization, which is given off rapidly on exposure to the air, leaving a salmon colored powder resembling litharge. On longer exposure to the air the substance turns brownish black, but this change does not take place, if it is kept in a desiccator. It begins to decompose at 215° (uncorr), therefore 10° above the decomposition point of iodoanilic acid. It is soluble in water forming a purple solution like that of iodoanilic acid, and is thrown out of this solution by the addition of sulfuric, or hydrochloric acid; boiling with water converts it into iodoanilic acid. It is much more soluble in alcohol than in water, and the solution shows a strong red color, in this respect also resembling iodoanilic acid; soluble in ether, acetone, ethyl acetate, glacial acetic acid, nitrobenzene, or aniline; nearly insoluble in cold, more soluble in hot chloroform, carbon disulfide, benzene, or toluene; essentially insoluble in naphtha, whether hot or cold. Toluene is the best solvent for it. Cold strong hydrochloric acid or sulfuric acid has no visible effect on it, but when heated an orange solution is formed, which remains unchanged on cooling. Hot, strong nitric acid oxidizes it vigorously with separation of iodine. Dilute sodium hydroxide forms a reddish purple solution.

Action of Hot Water on the Hemiether.—Two grams of the substance were warmed with water until they had dissolved completely, and the solution was then kept just below the boiling point for five minutes. After cooling, sulfuric acid was added, and the salmon colored precipitate crystallized twice from toluene and dried at 100°, when an analysis proved that it was iodoanilic acid, $C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.03. The iodoanilic acid thus prepared resembled the hemiether closely, for, when dissolved in hot toluene, it gave long, thin, red needles (although no spindles), and at a lower temperature red, diamond-shaped plates containing very loosely attached toluene of crystallization (but not truncated on the obtuse angles). These left a salmon-colored powder identical with that from the hemiether, if dried at ordinary temperatures, but the powder was red if heat was used. The rhombic crystals darkened if exposed to the air for some days, but remained unaltered in the desiccator. The iodoanilic acid decomposed at 205° (uncorr.), but this point was not definite enough to be used to distinguish it from the hemiether, so that in all our work we resorted to analysis of the free acid, purified as described above, in order to identify iodoanilic acid.

Sodium Salt of the Hemiether of Iodoanilic acid, $[C_6I_2(ONa)O(OHONa)]_2O$.—Owing to the very slight stability of the salt its preparation could not be achieved from the hemiether. Thus, 15 grams of the hemiether suspended in 20 cc. of water gave with 4 cc. of 10% sodium hydroxide solution a deep purple liquid, which was sodium iodoanilate ($C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.20). The same result was obtained, if enough sodium hydroxide was used to precipitate the salt at once ($C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.06). The sodium hydroxide, therefore, has split the hemiether into two molecules of iodoanilic acid; and it was the same with potassium hydroxide in the proportion of 4 molecules to one ($C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.35). Nor were we more successful when we avoided an excess of alkali by using one gram of the hemiether suspended in a saturated solution of it, and adding potassium hydroxide, so as to have one molecule for each molecule of the hemiether in this gram of it, but the alkali, instead of forming the monopotassium salt, converted the hemiether into potassium iodoanilate, until it was exhausted.

As, therefore, there was no hope of forming its salt from the free hemiether, we turned our attention to the compound obtained directly from iodoanil and sodium hydroxide, which must be the salt of the hemiether, because this substance is obtained from it by acidification. It was prepared as follows: Ten grams of iodoanil, suspended in a mixture of 15 cc. of alcohol and 30 cc. of water, were treated with 15 cc. of a 50% solution of sodium hydroxide. The iodoanil passed slowly into solution with evolution of heat, but upon shaking the liquid vigorously for several minutes the sodium salt began to separate, and seemed to be completely formed after standing for half an hour, when it was filtered out, and washed with alcohol to remove sodium hydroxide and iodide, then warmed with benzene to dissolve any unchanged iodoanil, after which it was air-dried for analysis.

This very unsatisfactory purification was all we could use owing to the instability of the salt. Boiling with water for a few minutes converted it into sodium iodoanilate ($C_6I_2(OH)_2O_2$, I, 64.78). Found, 64.90, while on longer boiling an odor of iodine was observed. Two crystallizations from alcohol and water also gave the iodoanilate ($C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.24) and washing with warm alcohol reduced its iodine by 10%.

Salt of the Hemiether Air Dried.—Subst., 0.4364, 0.4984. Loss at 100°, 0.0434, 0.0496.
Calculated $[C_6I_2(ONa)O(OHONa)]_2O.5H_2O$: H_2O, 9.13.
Found: H_2O, 9.95, 9.96.

Sodium Iodoanilate Air Dried.—Subst., 0.3926, 0.4750. Loss at 100°, 0.0792, 0.0962
Calculated $C_6I_2(ONa)_2O_2 6H_2O$: H_2O, 19.86.
Found: H_2O, 20.12, 20.25.

The sodium iodoanilate, therefore, contains twice as much water as the salt of the hemiether.

Salt of the Hemiether dried at 100°.
Calculated $[C_6I_2(ONa)O(OHONa)]_2O$: Na, 10.34; I, 57.09.
Found: Na, 9.85, 9.90, I, 55.90.

These results are as good as could be expected from a salt, which could be so little purified. $C_6I_2(ONa)_2O_2$ requires Na 10.55, I 58.24, so that the results would have to be much nearer to decide between these two formulas, but with our other observations they do establish the peculiar formula given above, as explained in the introduction.

Properties of the Sodium Salt of the Hemiether of Iodoanilic Acid.—It crystallizes in purple prisms terminated at each end by two planes at an obtuse angle. At 100° it loses its water of crystallization, and is converted into a black powder with a tinge of purple. It dissolves freely in water, and the solution might be mistaken for one of potassium permanganate; boiling this solution converts it into sodium iodoanilate; the salt of the hemiether is practically insoluble in alcohol, but decomposed by it when warm. Crystallization from a mixture of alcohol and water converts it into iodoanilate. An excess of sodium hydroxide precipitates it from its solutions.

These properties are essentially the same as those of sodium iodoanilate, except that when anhydrous it is dark brownish purple instead of black.

Action of Aniline on the Hemiether of Iodoanilic Acid.—Two grams of the hemiether dissolved in alcohol were treated with aniline drop by drop, until there was no further precipitation, and the light salmon colored product was washed with alcohol and dried *in vacuo.*

Calc. $C_6I_2(OHNH_2C_6H_5)_2O_2$ I, 43 82 Found. 43 34.

According to this analysis it is aniline iodoanilate, but its properties throw some doubt on this conclusion. The light salmon color is strange for an iodoanilate, and so are the facts that dilute sulfuric acid has no action on it, and sodium hydroxide very little in the cold; both, however, give iodoanilic acid if hot. More experimental work, therefore, is needed, before its nature can be considered settled.

If the hemiether was warmed with aniline it dissolved more quickly than in the cold, and the dark brown liquid deposited scales, which, after the addition of a little alcohol, were filtered, and washed with alcohol, when they were recognized as dianilinoquinone by the absence of halogen, the characteristic purple scales, and the carmine-red color with strong sulfuric acid, identical with the properties shown by a specimen of dianilinoquinone prepared in the usual way.

Diiododiacetoxyquinone, $C_6I_2(C_2H_3O_2)_2O_2$.—This substance was formed when 2 grams of the hemiether were mixed with acetic anhydride in the proportion of 1 molecule to 5, and the mixture warmed, until all the hemiether had gone into solution. A yellow solid was deposited as the liquid cooled, which was freed from most of the acetic anhydride by standing on a porous plate *in vacuo* over potassium hydroxide. It was then crystallized several times from a mixture of 3 parts naphtha and one part of benzene, and dried *in vacuo.*

Calculated $C_6I_2(C_2H_3O_2)_2O_2$: I, 53.34. Found: 53.87.

Properties of Diiododiacetoxyquinone.—It crystallizes from benzene and naphtha in brilliant square yellow plates, which begin to decompose at 190° giving off violet vapors, and melt at 270° (uncorr.). It is easily soluble in alcohol, ethylacetate, glacial acetic acid, carbon tetrachloride, benzene, or toluene, essentially insoluble in naphtha. Cold water saponifies it slowly, warm water quickly into iodoanilic acid; cold dilute sodium hydroxide saponifies it immediately.

That this substance was a derivative of iodoanilic acid and not of the hemiether was shown by the fact that it was identical in every respect with a specimen prepared earlier from acetic anhydride and iodoanilic acid.

Calculated $C_6I_2(C_2H_3O_2)_2O_2$: I, 53.34. Found: 53.51.

When the sodium salt of the hemiether was treated with acetyl chloride we obtained the free hemiether.

Calculated $[C_6I_2OHO_2]_2$: I, 66.32 Found: 66.58.

This experiment seems to show that acetyl chloride does not act easily on the hemiether.

Action of Hot Sodium Hydroxide on Iodoanil.—If the mixture of sodium hydroxide and iodoanil was boiled for a minute, the product was sodium iodoanilate.

Calculated $C_6I_2(OH)_2O$. I, 64.78 Found 65.25

Diiodohydroxyethoxyparaquinone, $C_6I_2(OH)(OC_2H_5)O_2$.—Ten grams of iodoanil were suspended in 50 cc. of alcohol, and treated in the cold with 10 cc. of a 50% solution of sodium hydroxide all in one portion. Upon shaking, the iodoanil went into solution rapidly with evolution of heat, and the greenish black liquid gave off a disagreeable penetrating smell like that observed in the preparation of the hemiether; three to four times its volume of water was then added, when upon acidification with dilute sulfuric acid a reddish orange precipitate was thrown down, which was washed with water till the filtrate began to turn purple, and then crystallized three times from naphtha. The diiodohydroxyethoxyquinone was dried at 80° for analysis.

In preparing this compound it is necessary to add the whole of the sodium hydroxide at once. If, instead, it is added in small portions at a time with shaking after each addition, the orange-red precipitate obtained on acidification did not crystallize from naphtha in the clusters of red needles, which show that the reaction has gone normally, but in small crystals, or sometimes it separated in an amorphous state. Such a product was separated by cold alcohol into two portions, the more soluble of which was the monoethylether, while the residue after crystallization from hot alcohol melted at 185° showing that it was the diiododiethoxyquinone.

Analyses of diiodohydroxyethoxyquinone.

Subst., 0.2300, 0.1836, 0.2110, 0.2076, 0.2508. AgI, 0.2658, 0.2092, 0.2382, 0.2348, 0.2822. Calc. $[C_6I_2OC_2H_5O_2]_2O$: I, 61.78; $C_6I_2OHOC_2H_5O_2$: I, 60.42. Found: I, 62.47; II, 61.59; III, 61.02; IV, 61.14; V, 60.82.

The specimens used in I and II were crystallized 3 times, those in III and IV 6, that in V 8 times.

Properties of Diiodohydroxyethoxyquinone.—It crystallizes from naphtha in rosettes of brilliant long red needles, which after several days exposure to the air lose their luster and turn reddish black, but remain unchanged in the desiccator. It begins to decompose at 160°, but does not melt completely till 180° (uncorr.). It is soluble in alcohol, ether, chloroform, tetrachloride of carbon, glacial acetic acid, carbon disulfide, benzene, toluene, ethylacetate or nitrobenzene, almost insoluble in cold, soluble in hot naphtha; water in the cold dissolves it slowly forming a purple solution, in boiling water it dissolves easily, but if the solution is boiled a short time decomposition takes place attended with separation of iodine and the formation of a dark brown solution. Strong hydrochloric acid produces no visible effect on it; strong sulfuric acid dissolves it with a dark brown color; strong nitric acid, if gently warmed, decomposes it with separation of iodine. The action of alkalies is described in detail in the following sections.

Potassium Salt of Diiodohydroxyethoxyquinone, $C_6I_2(OK)(OC_2H_5)O_2H_2O$.—Two grams of the monoethyl compound were treated in the cold with an excess of a 10% solution of potassium hydroxide, when, after standing for several minutes, a black mass was precipitated, which, although nearly insoluble in the excess of alkali, imparted a pink color to the liquid. The solid was freed from potassium hydroxide by washing with a small quantity of water, until it began to dissolve, after which the washing was continued with a few drops of alcohol, and the purification concluded by crystallization from alcohol twice for I and III, four times for II.

Subst., 0.2298, 0.1566, 0.6758, AgI, 0.2284, 0.1552; K_2SO_4, 0.1206 Calc. for $C_6I_2OKOC_2H_5O_2$: I, 55.42; K, 8.54; for $C_6I_2OKOC_2H_5O_2H_2O$ I, 53.33; K, 8.21; for $[C_6I_2(OK)(OC_2H_5)O(OKOH)]_2O$: I, 54.38; K, 8.37 Found I, I, 53.72; II, 53.57; K, III, 8.01.

It was impossible to determine experimentally, whether water of crystallization was retained at 100°, as it decomposed slowly, when heated to higher temperatures.

The same compound was also obtained as follows: Ten grams of iodoanil, suspended in 80 cc. of alcohol, were treated with 20 cc. of a solution of 15 grams of potassium hydroxide in 100 cc. of alcohol. The iodoanil dissolved immediately, and after being heated just below boiling for several minutes the solution changed from dark reddish purple to blackish purple. It was then allowed to stand at rest, and, if the experiment had succeeded, the solution was converted in a few minutes into a mass of blac[illegible]stals, which were washed with a little alcohol, and then after war[illegible] with successive portions of benzene, until no more color was rem[illegible], were recrystallized three times from alcohol, and dried at 100°.

Subs[illegible].2028, 0.1896, 0 2356. 0.3752; AgI, 0.2022, 0.1888, 0 2328; K_2SO_4, 0 0632.
Calc. for $C_6I_2OC_2H_5OKO_2H_2O$: I, 53 33; K, 8.21. Found: I, 53 88, 53.82, 53.39; K, 7.56.

This formation of the potassium salt direct from iodoanil cannot be recommended as a method for its preparation, since the conditions, under which it takes place, are so delicately balanced that the process frequently miscarries. If the first solution of the iodoanil was greenish instead of reddish black, the product was more or less contaminated with either potassium iodoanilate ($C_6I_2(OH)_2O_2$, I, 64.78; found, 63.98) or diiododiethoxyquinone, which was precipitated as an orange-red compound, sometimes the only product of the reaction, identified by its melting point 186° after several crystallizations from alcohol.

Properties of the Potassium Salt of Diiodohydroxyethoxyquinone.—It crystallizes from alcohol in bluish black needles, which are black after drying. It dissolves freely in water forming a dark solution much like that of potassium permanganate, which is not alkaline to test paper, and does not become so even after boiling for several minutes. Potassium hydroxide precipitates it from this solution, even when present in comparatively small amount, but on warming the mixture potassium iodoanilate is formed. It is slightly soluble in cold alcohol, freely in hot; insoluble in ether, chloroform, naphtha, benzene, or toluene; essentially insoluble in cold nitrobenzene, or aniline, but dissolves on warming; soluble in acetone, ethylacetate, or glacial acetic acid. Alcohol is the best solvent for it, as crystallization from this substance is not attended by perceptible decomposition. Dilute acids set free the diiodohydroxyethoxyquinone. Strong nitric acid acts on it with sufficient violence to set it on fire. With alcoholic sodium ethylate the black salt forms a yellow solution, from which acid throws down a white precipitate evidently a hemiacetal, since it turns orange-red on gentle warming with dilute sulfuric acid.

Attempts to Make the Sodium Salt.—None of our attempts to make the sodium salt by the methods, which had furnished the potassium salt easily, led to the desired result. Thus when the free substance was treated in the cold with a few drops of a 10% solution of sodium hydroxide, sodium iodoanilate was formed ($C_6I_2(OH)_2O_2$, I, 64.78; found, 65.14). The same result was obtained, when the substance was heated with successive small portions of dilute sodium hydroxide (found, 64.99).

Ten grams of iodoanil suspended in 50 cc. of alcohol and gently warmed with 15 cc. of a saturated alcoholic solution of sodium hydroxide gave a greenish black solution, from which water threw down a precipitate of diiododiethoxyquinone, identified by its melting point, 186°. If methyl alcohol was used as the solvent, much heat was given out by the reaction, and water added to the hot solution precipitated diiododimethoxyquinone recognized by its orange-red color and melting point 195°; but if the solution was cooled, and then acidified, a white precipitate was obtained, shown to be the diiododimethoxyquinonedimethylhemiacetal of Torrey and Hunter[1] by its solubility in sodium hydroxide solution, and the great ease with which heat, or a dilute acid converted it into the diiododimethoxyquinone melting at 195°.

We finally succeeded in preparing a pure solution of the sodium salt by treating the silver salt with sodium chloride, but we did not obtain it in the solid state.

Silver Salt of Diiodohydroxyethoxyquinone $C_6I_2(OAg)(OC_2H_5)O_2$.—A specimen of the potassium salt which had been crystallized once from alcohol, was dissolved in water, and treated with a solution of silver nitrate until there was no further precipitation. The brown solid thus obtained was washed by decantation, until it was free from silver nitrate, and dried on a porous plate in a desiccator.

Subst, 0.2126; AgI, 0.1894. $[C_6I_2OC_2H_5OAgOHO]_2O$: I, 47.38, $C_6I_2OC_2H_5OAgO_2$, I, 48.19. Found: 48.16.

A specimen dried at 100° turned somewhat purple, which was evidently due to decomposition, as it contained 1% more iodine than the salt analyzed above.

Properties of the Silver Salt of Diiodohydroxyethoxyquinone.—It is a brown solid, which is somewhat decomposed, if dried at 100°. It is very slightly soluble in water forming a light purple solution; insoluble in cold alcohol, barely soluble in hot. Cold dilute nitric acid does not act on it, but when hot decomposes it with formation of silver iodide. Potassium hydroxide does not act in the cold, but on warming gives a brownish red solution and silver oxide. Ammonium hydroxide dissolves it easily forming a red solution. Potassium chloride gives silver chloride and the potassium salt recognized by its bluish black color and solubility in alcohol; sodium chloride in saturated solution acts in the same way. The solution of the sodium salt was dark purple. It was more soluble in alcohol than the potassium salt.

When the silver salt was heated with ethyl bromide in a sealed tube at 100° for 6 to 8 hours, silver bromide was formed, and the other product, which was orange-red, was freed from the excess of ethyl bromide by spontaneous evaporation, and then crystallized 7 times from alcohol, when it showed the melting point 183°. The amount left was too small for further crystallization, or analysis, but we think it safe to infer that it was diiododiethoxyquinone which melts at 186°. Frequently iodoanilic acid appeared also in these experiments. When the potassium salt was heated to 100° for 36 hours with ethyl bromide, a little diiododiethoxyquinone was formed, but the yield was exceedingly small.

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[1] THIS JOURNAL, 34, 702 (1912).

An aqueous solution of the potassium salt ($C_6I_2OC_2H_5OKO_2$) gave, after standing an hour with barium nitrate, a small bluish black precipitate of the barium salt, which proved to be moderately soluble in water, or alcohol. With calcium nitrate no precipitate was formed, but on the addition of alcohol a small amount of a bluish black calcium salt was obtained. The copper salt was light green.

Diiodohydroxyethoxyquinonethylhemiacetal.—When an alcoholic solution of sodium ethylate was added to diiodohydroxyethoxyquinone in very small quantities at a time, a blackish purple mass was formed at first, but upon adding more of the sodium ethylate the whole went into solution with an orange-brown color, and then the addition of a dilute acid threw down a white precipitate, which could be dissolved in sodium hydroxide, and reprecipitated with dilute acid. No attempt was made to analyze it, as its instability forbade thorough purification, even the best specimens we obtained showing an orange tint. That it was the expected hemiacetal, however, was shown by its properties, and especially by its decomposition with dilute acid, which on gentle warming converted it into an orange-red compound, and this after 5 crystallizations from naphtha was proved to be the diiodohydroxyethoxyquinone.

Subst., 0.2090, 0.2760; AgI, 0.2354, 0.3108 Calc $C_6I_2OC_2H_5OHO_2$ I, 60.45 Found: I, 60.88, 60.87.

It would seem from these results that the conversion into the hemiacetal was an excellent method of purifying the diiodohydroxyethoxyquinone.

Properties of Diiodohydroxyethoxyethylhemiacetal.—It is probably white when pure, but we did not succeed in obtaining it dry without an orange tint. It is soluble in alcohol, ether, chloroform, ethyl acetate, or benzene; esssentially insoluble in naphtha, carbon disulfide, toluene, or water; on warming with water an orange-red solid is obtained, and the liquid is colored dark purple by iodoanilic acid. When heated to 100°, it is converted into the diiodohydroxyethoxyquinone, and the same change is brought about by gentle warming with dilute acids. In fact, the substance shows a strong tendency to lose alcohol under most conditions. Acetic anhydride forms with it a red solution. It dissolves easily in sodium hydroxide forming the sodium salt, but this was so soluble that we made no attempt to isolate it.

The Aniline Salt of Diiodohydroxyanilinoquinone,

$C_6I_2(NHC_6H_5)(OHNH_3C_6H_5)O_2$.

—When 2 grams of diiodohydroxyethoxyquinone, dissolved in 25 cc. of alcohol, were treated with aniline, the first few drops produced a vivid dark purple color, and, if the addition of the aniline was continued, until the color ceased to become deeper, after a short time rosettes of brownish purple needles were deposited slowly in the cold, at once when hot, and the dark color disappeared from the solution. The salt was purified by washing with alcohol.

Calculated $C_6I_2NHC_6H_5OHNH_2C_6H_5O_2$: I, 45.33. Found: I, 45.22, 45.52.

Properties of the Aniline Salt.—In its preparation it is obtained from alcohol in rosettes of brownish purple needles, which begin to decompose at 165°, but do not melt even at 285°. It is soluble in ether, acetone, chloroform, ethylacetate, or glacial acetic acid; essentially insoluble in cold alcohol, tetrachloride of carbon, naphtha, benzene, toluene, or nitrobenzene, but dissolves in any of these solvents when hot; insoluble in water. The solutions are purple, but we found it impossible to crystallize the salt without decomposition from any of its solvents. Dilute acids set free the diiodohydroxyanilinoquinone. Hot strong nitric acid oxidizes it setting free iodine. The action of acetic anhydride will be described later.

Diiodohydroxyanilinoquinone, $C_6I_2(OH)(C_6H_5NH)O_2$.—Two grams of the aniline salt were treated with 30 cc. of dilute sulfuric acid, when the color changed at once to a deep blue turning black in a few minutes. The filtrate was proved to contain aniline by treatment with bromine. The solid after washing with water and finally with a little alcohol was recrystallized several times from toluene and, dried at 100°.

Subst., 0.2068, 0.2345; AgI, 0.2066, 0.2362. Calc. $C_6I_2OHC_6H_5NHO_2$: I, 54.37.
Found: 54.00, 54.45.

Properties of Diiodohydroxyanilinoquinone.—It forms very small navy blue crystals, which decompose at about 190°. It is slightly soluble in alcohol, chloroform, glacial acetic acid, benzene, toluene, or nitrobenzene; easily soluble in ether, ethyl acetate, or acetone; essentially insoluble in naphtha, or in cold carbon disulfide, soluble in the latter when hot. Hot nitric acid forms an orange-red solution with it. Sodium hydroxide dissolves it forming a dark red solution of the salt, from which an acid throws down the original substance. This sodium salt could be obtained as a dark red solid by treating the free compound with ether and sodium ethylate; it is freely soluble in water, or alcohol, and is converted by exposure to the air into a blackish red tar. The pyridine salt is brown. The free hydroxy compound, when suspended in alcohol and treated with bromine water, forms an orange solution, which gives a yellow precipitate on dilution.

When the aniline salt $C_6I_2(C_6H_5NH)(OHNH_2C_6H_5)O_2$ was warmed with acetic anhydride a dark blue solution was formed solidifying on cooling to a mass of dark blue crystals, which after crystallization from benzene and naphtha began to decompose at about 170°, and were soluble in most of the organic solvents except naphtha. We believe the substance to be diiodoacetoxyanilinoquinone from the following observations. With warm sodium hydroxide it formed a dark red solution, and, if heated with aniline, gave dianilinoquinone (recognized by the absence of iodine), its brown color, scale-like crystals from nitrobenzene, and the crimson solution with strong sulfuric acid, being identical in all these respects with a specimen prepared in the usual way.

Diiodoacetoxyethoxyquinone, $C_6I_2(OC_2H_3O)(C_2H_5O)O_2$.—Two grams of the diiodohydroxyethoxyquinone were heated with acetic anhydride in the proportion of one molecule to five, until the whole had gone into solution, when on cooling orange-red crystals were deposited, which, after being freed from acetic anhydride *in vacuo*, were purified by 5 crystallizations from naphtha, and dried at 100°.

Subst., 0.2400, 0.2030; AgI, 0.2454, 0.2082. Calc. $C_6I_2OC_2H_3OOC_2H_5O_2$: I, 54.95.
Found: I, 55.27, 55.44.

Properties of Diiodoacetoxyethoxyquinone.—Brilliant orange-red prisms which melt at 166° (uncorr.) without decomposition. It is soluble in alcohol, ether, chloroform, acetone, ethylacetate, glacial acetic acid, carbon disulfide, benzene, toluene, or nitrobenzene; nearly insoluble in cold naphtha; insoluble in water. Sodium hydroxide converts it into sodium iodoanilate slowly when cold, rapidly when hot. The best solvent for it is hot naphtha.

Although the free substance reacted so easily with acetic anhydride, strangely enough the dry potassium salt was not affected by it in the cold, and gave a black varnish with it on long heating. Acetylchloride in excess converted the salt into diiodohydroxyethoxyquinone (calculated I, 60.45; found, 61.28). As the conversion was complete, it could hardly have been caused by an impurity of hydrochloric acid. It is strange, however, that the excess of acetylchloride did not act on the free hydroxy compound under conditions which gave complete reaction with the anhydride; and also no result was obtained, even when a drop of strong sulfuric acid or a little sodium acetate was used as a catalyzer.

Action of Aniline on Diiodoacetoxyethoxyquinone.—Three grams of the diiodoacetoxyethoxyquinone were dissolved in warm alcohol, and, after the solution had cooled, 2 cc. of aniline were added, when the liquid turned dark red immediately, and deposited a greenish black solid, which was washed with alcohol, as it is only slightly soluble in the cold. Upon treatment with hot alcohol the product was separated into a more soluble black compound, and one which was yellowish brown and nearly insoluble. The black substance, which is the principal product in the cold, was purified by crystallization from alcohol, and dried at 90°.

Subst., 0.2250, 0.1988; AgI, 0.2433, 0.1890. Calc. $C_6I_2NHC_6H_5OC_2H_5O_2$: I, 51.31.
Found: I, 51.57, 51.39.

Properties of Diiodoethoxyanilinoquinone.—It crystallizes from alcohol in long black shining needles, which melt at 182° (uncorr.) with decomposition.

It is soluble in ether, chloroform, acetone, acetic ester, carbon disulfide, benzene, toluene, or nitrobenzene, forming dark purple solutions; slightly soluble in cold, soluble in hot alcohol, which is the best solvent for it. Strong sulfuric acid gives a greenish black solution, turning brownish on standing, sodium hydroxide does not act in the cold, but on warming forms a red solution from which an acid throws down a black substance probably diiodohydroxyanilinoquinone.

The yellowish brown product separated from the preceding by its slight solubility in hot alcohol was formed in small quantity in the cold, but became the principal product, if the aniline was added to a hot alcoholic solution of diiodoacetoxyethoxyquinone. It was purified by crystallization from toluene.

Subst , 0.1868, AgI, 0 1623. Calc. $C_6I_2(NHC_6H_5)_2O_2$ I, 46 86. Found· I, 46 94

Properties of Diiododianilinoquinone.—It crystallizes from toluene in dark brown needles decomposing at about 220°. It is slightly soluble in chloroform, acetone, acetic ester, benzene, toluene, nitrobenzene, or aniline, more soluble hot; essentially insoluble in alcohol, ether, carbon disulfide, glacial acetic acid, or naphtha. It is decomposed on warming with sodium hydroxide forming a yellow solution, which with bromine water gives a precipitate of tribromoaniline. The best solvent for it is hot toluene.

Action of Sodium Hydroxide on Bromoanil in Ethyl Alcohol.—Ten grams of bromoanil suspended in 50 cc. of ethyl alcohol were treated with 10 cc. of 50% aqueous sodium hydroxide solution; the solid dissolved at once, and soon deposited purple needles of sodium bromoanilate, recognized by the analysis of the free acid after it had been crystallized several times from toluene ($C_6Br_2(OH)_2O_2$, Br 53.69, found Br 53.65). The experiment was repeated several times under varying conditions, but in every case the product was sodium bromoanilate.

In the hope of getting α or β addition compounds similar to those obtained from tetrabromoorthoquinone iodoanil, or bromoanil was allowed to stand for 5 months with methyl alcohol, but no action was observed.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 231.]

RESEARCHES ON QUINAZOLINES. XXXII. ON SOME QUINAZOLONES, BENZIMIDAZOLES, AND RELATED COMPOUNDS, DERIVED FROM *s*-PSEUDOCUMIDINE.

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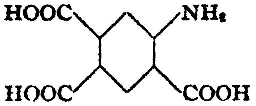
1. Introduction, and Discussion of Results.

In continuation of the investigations which have been going on for several years in this laboratory on heterocyclic systems obtainable from various *o*-amino compounds,[1] we have endeavored to prepare for study the 5-amino-1,2,4-benzene tricarboxylic acid(I), since it presents an interesting combination of an anthranilic with an *o*-phthalic structure, and further because none of the six possible aniline tricarboxylic acids have as yet been described in the literature.



(I)

Two lines of approach have been followed towards this goal: (1) *s*-pseudocumidine was acetylated and the acetyl derivative oxidized; (2) pseudocumene was converted into the 5-nitro derivative, the nitro pseudocumene oxidized to the nitro tricarboxylic acid, and the latter reduced. Unfortunately, serious obstacles have been encountered on both paths.

On the first route, the chief obstacle proved to be the oxidation of the acetpseudocumidide. Although we tried various oxidizing agents, under varied conditions, only once did we obtain any of the acid sought, and then only in sufficient amount to carry out a few superficial tests. Plenty of the mono- and dibasic acids were separated, but it seemed impossible to oxidize all three methyl groups without simultaneously destroying the entire molecule, irrespective of whether the initial material was pseudocumidide, mono- or dibasic acid. This was decidedly disappointing, in view of the fact that both amino *o*-phthalic acids are fairly stable compounds,[2] as well as the *p*-diamino terephthalic and the 4,6-diamino isophthalic acids,[3] and we had no difficulty in preparing this latter acid by oxidation of the corresponding diacetaminoxylene, or in oxidizing 2,4-diacetaminotoluene to the corresponding diacetaminobenzoic acid.[4]

Jannasch and Weiler[5] met with similar difficulties in attempting to oxidize isodurene, $C_6H_2(CH_3)_4$. When the oxidation was conducted in acetic acid solution with chromic anhydride, part of the hydrocarbon was unattacked, and part was burned to carbon dioxide and water. With very dilute potassium permanganate solution, mono- and dibasic acids were produced, but no tetracarboxylic acid. On the other hand, Mills[6] obtained a yield of 85–88% of pyromellitic acid, $C_6H_2(COOH)_4$, when he oxidized durylic acid, $(CH_3)_3C_6H_2COOH$, with dilute alkaline potassium permanganate solution.

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[1] Bogert, *et al.*, THIS JOURNAL, 32, 784, 1297, 1654 (1910); 33, 949 (1911); 34, 183, 516, 524, 683, 1569, 1576 (1912).

[2] Bogert and Renshaw, THIS JOURNAL, 30, 1135 (1908); Bogert and Jouard, *Ibid.*, 31, 483 (1909).

[3] Bogert and Kropff, *Ibid.*, 31, 842 (1909).

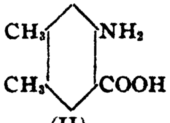
[4] Bogert, Amend and Chambers, *Ibid.*, 32, 1299 (1910).

[5] *Ber.*, 27, 3443 (1894).

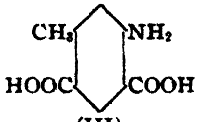
[6] *J. Chem. Soc.*, (*London*) 101, 2193 (1912).

By the second route, we travelled fairly smoothly to the point reached by Schultz and Herzfeld,[1] namely the production of the nitro tricarboxylic acid by oxidation of nitropseudocumene; but there our difficulties began, and we have not yet succeeded in getting any satisfactory reduction of this nitro acid to the amino acid.

Pending further experiments in the production of the tricarboxylic acid, we turned our attention to the mono- (II) and dibasic (III) acids obtained by the partial. oxidation of the acetpseudocumidide.



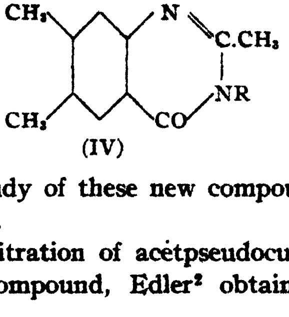
(II)



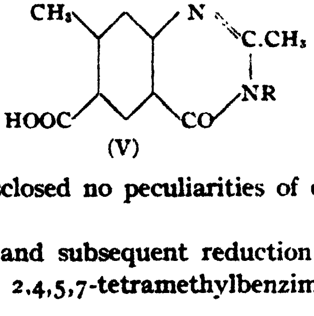
(III)

The configuration of these acids indicates that in the oxidation of acetpseudocumidide, under the conditions of our experiments, the methyl group in position 4 is first attacked, and then that at 2.

As both of these are of anthranilic type, they yielded acetyl anthranils and 4-quinazolones of types IV and V:



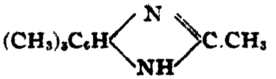
(IV)



(V)

A study of these new compounds disclosed no peculiarities of especial interest.

By nitration of acetpseudocumidide and subsequent reduction of the nitro compound, Edler[2] obtained the 2,4,5,7-tetramethylbenzimidazole (VI):



$$(CH_3)_3C_6H\langle{}^{N}_{NH}\rangle C.CH_3 \qquad \text{(VI)}$$

We have repeated his work and in addition have prepared a number of new derivatives of this imidazole, including the phthalones.

The propionyl derivative of pseudocumidine is also described in the following pages, together with the benzimidazoles and other compounds obtained from it. By a Friedel-Crafts reaction, the chloroacetyl group was introduced but, unfortunately, as Kunckell[3] has shown in the case of the acetyl derivative, this group enters in position 3, instead of 6, so that the resulting ketone could not be used for the preparation of substituted indigos.

[1] *Ber.*, 42, 3607 (1911).

[2] *Ibid.*, 18, 630 (1885).

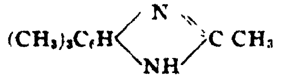
[3] *Ibid.*, 33, 2652 (1900).

2. Experimental.

5-Pseudocumidine(5-amino-1,2,4-trimethylbenzene) was acetylated by the action of acetic anhydride upon its solution in glacial acetic acid. The crude product (yield, 96%) was purified by recrystallization from 50% acetic acid, and then formed long colorless needles, melting at 164.5° (corr.). Auwers[1] gives the melting point as 164°.

This pseudocumidide was dissolved in glacial acetic acid and nitrated at low temperature with fuming nitric acid, giving the 6-nitro derivative in small colorless glassy needles, which were recrystallized until the melting point remained constant at 199.5° (corr.). Edler[2] gives the melting point as 193–4°, and Auwers[3] as 202–4°.

By reduction of this nitro acetamino compound, the benzimidazole[4]



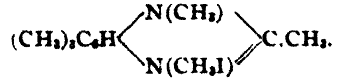
$$(CH_3)_3C_6H\begin{matrix}\diagup N \diagdown \\ \diagdown NH \diagup\end{matrix}C\,CH_3$$

was obtained in minute colorless silky needles, melting at 232° (corr.).

2,4,5,7-Tetramethylbenzimidazole Iodomethylate, $C_{11}H_{14}N_2.CH_3I$.—Four grams of the above imidazole were dissolved in 200 cc. of benzene, 15 cc. of methyl iodide added, and the solution boiled for five hours under a reflux condenser. The crude product was recrystallized from 50% alcohol, giving minute colorless needles, which darken above 330°, but remain unmelted at 350°, and are insoluble in ether.

Subst. 0.2768, 0.2040; 22 cc. N_2 (19° and 750 mm. over H_2O), 0.1526 AgI.
Calculated for $C_{12}H_{17}N_2I$: N, 8.87; I, 40.14 Found: N, 8.97; I, 40.41.

1,2,4,5,7-Pentamethylbenzimidazole Iodomethylate,



$$(CH_3)_3C_6H\begin{matrix}\diagup N(CH_3) \diagdown \\ \diagdown N(CH_3I) \diagup\end{matrix}C.CH_3.$$

—Five grams of the above tetramethylbenzimidazole, four grams of metallic sodium, 20 cc. of methyl iodide, and 200 cc. of dry xylene, were

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[1] *Ber.*, 18, 2661 (1885).

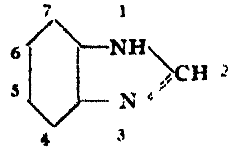
[2] *Ibid.*, 18, 629 (1885).

[3] *Loc. cit.*

[4] Edler, *Loc. cit.*

This compound is not listed in Richter's *Lexikon*, nor in Kuehling's *Handbuch der Stickstoffhaltigen Orthocondensationsproducte*. In Beilstein's *Handbuch*, it is not in its proper place in Vol. IV, but appears merely as an anhydro base under the nitro acetpseudocumidine (II, 552).

For convenience of reference, the positions on the benzimidazole nucleus will be indicated in the following pages according to the system adopted in Richter's *Lexikon*,



boiled together for six hours under a reflux condenser. The iodomethylate separated gradually. After cooling and removal of excess of metallic sodium, the crude iodomethylate was crystallized several times from 50% alcohol, and was thus obtained in minute straw-colored crystals, melting at 274–5° (corr.). Yield, 5 g.

It is soluble in water, alcohol, chloroform, carbon tetrachloride or pyridine; practically insoluble in ether, benzene or ligroin.

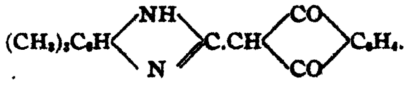
Subst. 0.2336, 0.2009; 17.80 cc. N_2 (21° and 749 mm. over H_2O), 14.5 cc. N_2 (18° and 763.4 mm. over H_2O).
Subst. 0.2485; AgI, 0.1801.
Calculated for $C_{13}H_{19}N_2I$: N, 8.48; I, 38.45. Found: N, 8.51, 8.33; I, 38.89.

2-Cinnamenyl-4,5,7-trimethylbenzimidazole, $(CH_3)_3C_6H[N_2H]C.CH : CH.C_6H_5$.—An intimate mixture of six grams of 2,4,5,7-tetramethylbenzimidazole and 3.9 grams of benzaldehyde was heated for two hours at 180°. When cold, the crystalline mass was washed carefully with small portions of cold alcohol and then crystallized from the same solvent. It was thus obtained as a colorless crystalline solid, melting at 257.5° (corr.), insoluble in ligroin or ether.

Subst. 0.2077; 19.2 cc. N_2 (13° and 760 mm. over H_2O).
Calculated for $C_{18}H_{18}N_2$: N, 10.70. Found: N. 10.87.

2-p-Nitrocinnamenyl-4,5,7-trimethylbenzimidazole, $(CH_3)_3C_6H[N_2H]C.CH : CH.C_6H_4.NO_2(p)$, was prepared in a similar manner by heating for two hours at 210° an intimate mixture of six grams (one mole) of the tetramethylbenzimidazole with 5.17 grams (one mole) of *p*-nitrobenzaldehyde. The cold crystalline melt was pulverized, washed repeatedly with small portions of cold alcohol, and finally crystallized from hot alcohol. It separated as a yellow powder, darkening at 280°, and melting at 303–5° (uncorr.); easily soluble in isoamyl alcohol, chloroform or acetone; difficultly soluble in ether or benzene; and practically insoluble in ligroin, carbon tetrachloride or carbon disulfide.

2,4,5,7-Tetramethylbenzimidazole Phthalone,



$$(CH_3)_3C_6H\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle C.CH\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4.$$

—Tetramethylbenzimidazole (5.8 g.) and phthalic anhydride (4.36 g.) were intimately mixed and the mixture heated for three hours at 180°. The cooled vitreous melt was extracted with hot 95% alcohol and, as these filtered extracts cooled, the phthalone separated in yellow crystals. The product was recrystallized until its melting point remained constant at 296–7° (corr.). Yield, 2.8 g. This phthalone is readily soluble in isoamyl alcohol or chloroform; slightly soluble in ether, carbon tetrachloride, acetone, ethyl acetate or benzene; and insoluble in ligroin or cold aqueous alkalies.

Subst. 0.1893; 15.3 cc. N_2 (22° and 762 mm. over H_2O).
Calculated for $C_{18}H_{17}O_2N_2$: N. 9.21. Found: N, 9.15.

Propionopseudocumidide, $(CH_3)_3C_6H_2NH.CO.C_2H_5$, was prepared by the direct action of propionic anhydride upon pseudocumidine. The crude product crystallized from 50% acetic acid in colorless needles, melting at 144° (corr.). Yield, 36 grams from 30 grams of the pseudocumidine. It was also prepared by dissolving the pseudocumidine in glacial acetic acid, adding the calculated amount of propionic anhydride, heating the solution to boiling, and diluting with water. On cooling, the propionyl derivative crystallized out practically pure. It is easily soluble in alcohol, acetone, chloroform or carbon tetrachloride; moderately soluble in ligroin, ether or benzene; difficultly soluble in water.

Subst. 0 2246, 14.7 cc. N_2 (20° and 761 mm. over H_2O)
Calculated for $C_{12}H_{17}ON$ N. 7 33 Found 7.40.

6-Nitro-5-propionamino-1,2,4-trimethylbenzene, $(CH_3)_3C_6H(NO_2)NH.CO.C_2H_5$.—Ten cc. of fuming nitric acid were cooled to —12°, and six grams of the above propionyl derivative added slowly. After standing for a short time, the solution was poured into ice-water, and the precipitated nitro compound crystallized from alcohol. Yield, 6.5 g.

The pure substance forms minute colorless, prismatic crystals, melting at 167° (corr.); easily soluble in isoamyl alcohol, acetone, chloroform, carbon tetrachloride, benzene or pyridine; slightly soluble in ligroin or ether; and practically insoluble in carbon disulfide. Boiled for three hours with 20% hydrochloric acid, under a reflux condenser, it dissolved gradually, but separated unchanged as the solution cooled.

Subst 0.1576; 16.6 cc. N_2 (20° and 758 mm. over H_2O).
Calculated for $C_{12}H_{16}O_3N_2$: N, 11.88. Found: N. 11.95.

2-Ethyl-4,5,7-trimethylbenzimidazole, $(CH_3)_3C_6H[N_2H]C.C_2H_5$. — Ten grams of the above nitropropionamino compound were mixed with 30 cc. of concentrated hydrochloric acid, and granular tin added in small portions. The reduction proceeded smoothly. At its conclusion, the solution was filtered from excess of tin and the hydrochloride of the base precipitated by adding concentrated hydrochloric acid. Yield, 6.8 g. This salt is soluble in water, but is insoluble in strong hydrochloric acid. It dissolves also in alcohol or pyridine, but not in ether, ligroin, chloroform, carbon tetrachloride, acetone or benzene. It melts with decomposition at 318–20° (corr.).

Subst. 0.2508; 27.4 cc N_2 (19° and 753 7 mm over H_2O).
Calculated for $C_{12}H_{17}N_2Cl$· N, 12 39. Found: N, 12.47

By the action of alkalies upon an aqueous solution of the hydrochloride, the free imidazole was precipitated. Recrystallized from dilute alcohol, it formed minute colorless glassy crystals, melting at 197° (corr.). soluble in isoamyl alcohol, ether, chloroform, carbon tetrachloride, acetone, carbon disulfide, benzene or pyridine, and practically insoluble in ligroin.

Subst. 0.1828; 24.9 cc. N_2 (21° and 756.8 mm. over H_2O).
Calculated for $C_{12}H_{16}N_2$: N, 15.45. Found: N, 15.39.

Chloroplatinate.—Yellowish powder, very slightly soluble in water; decomposes with evolution of hydrogen chloride at 245–6° (corr.).

Subst. 0.1865; Pt, 0.0460.
Calculated for $(C_{12}H_{16}N_2)_2H_2PtCl_6$: Pt, 24.79. Found: Pt, 24.66.

Iodomethylate.—Five grams of the imidazole were dissolved in 200 cc. of benzene, 10 cc. of methyl iodide added, and the solution boiled under a reflux condenser. The iodomethylate separated gradually as a colorless crystalline precipitate. It was purified by recrystallization from 80% alcohol and then appeared in minute colorless needles, which darken above 300°, and melt with decomposition at 345–6° (corr.). The compound is insoluble in benzene, and but slightly soluble in ether.

Subst. 0.2343; 17 8 cc. N_2 (21° and 753 mm. over H_2O).
Subst. 0.2020; AgI, 0.1467.
Calculated for $C_{13}H_{19}N_2I$: N, 8.48; I, 38.44. Found: N, 8.53; I, 39.22.

3-Chloroacetyl-5-propionamino-1,2,4-trimethylbenzene, $(CH_3)_3C_6H(CO.CH_2Cl)NH.CO.C_2H_5$.—Ten grams propionopseudocumidide, 16 grams chloroacetyl chloride, and 200 cc. of carbon disulfide, were mixed in a flask and 60 grams of powdered aluminum chloride added gradually in small portions, shaking the flask well between additions. A copious evolution of hydrogen chloride ensued and the ketone separated as a flocculent solid. After all the aluminum chloride had been added, the mixture was allowed to stand for twelve hours. The carbon disulfide was then removed by decantation, followed by warming and exhausting, ice was added to the residue in the flask, the ketone filtered out and recrystallized from alcohol. Fine silky needles, melting at 181° (corr.), were obtained. Yield, 13.5 g. The substance is easily soluble in chloroform, carbon tetrachloride, isoamyl alcohol, acetone or pyridine, moderately soluble in ether or benzene, and practically insoluble in ligroin.

Subst. 0.2246; AgCl, 11.96.
Calculated for $C_{14}H_{18}O_2NCl$: Cl, 13.25. Found: Cl, 13.16.

Boiling for a few minutes with 20% hydrochloric acid splits off the propionyl group, giving the chloroacetyl pseudocumidine, which has been described already by Kunckell.[1]

Graebe[2] found that the chlorine of ω-chloroacetophenone could be easily converted into the corresponding acetate by boiling with an alcoholic solution of lead acetate, or into the corresponding alcohol by boiling with an aqueous solution of sodium carbonate or with lead hydroxide.

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[1] *Ber.*, 33, 2652 (1900).

[2] *Ibid.*, 4, 35 (1871).

The chlorine in the chloroacetyl propionopseudocumidide, we could not displace by similar treatment.

3-Chloroacetyl-5-propionoamino-6-nitro-1,2,4-trimethylbenzene, $(CH_3)_3C_6(NO_2)(COCH_2Cl)NH.CO.C_2H_5$.—Ten cc. of fuming nitric acid were cooled to —12°, and five grams of the chloroacetyl propionopseudocumidide added slowly in small portions.[1] The resulting solution was poured into ice-water, the precipitated nitro compound filtered out and crystallized from dilute alcohol, giving colorless fine silky needles, melting at 193.2° (corr.). Yield, 3.2 g. It is readily soluble in chloroform, isoamyl alcohol, acetic acid, acetone, benzene or pyridine; moderately soluble in ether or carbon tetrachloride; and practically insoluble in ligroin.

Subst. 0.1829; 14.8 cc. N_2 (22° and 754 mm. over H_2O).
Calculated for $C_{14}H_{17}O_4N_2Cl$: N, 8.96. Found: N, 9.04.

3,4-Dimethyl-6-acetoaminobenzoic acid, $(CH_3)_2C_6H_2(NH.COCH_3)COOH$. —In the oxidation of acetopseudocumidide by potassium permanganate described beyond, some of this monobasic acid was usually encountered. It is much more soluble in hot water, or in 50% acetic acid, than the accompanying methylacetoaminoisophthalic acid, and this difference in solubilities was made use of to separate the two acids. The pure monobasic acid forms minute colorless crystals, which melt with decomposition at 248–50° (corr.). It is soluble in alcohol or acetone; practically insoluble in ligroin, chloroform, carbon tetrachloride, ether, carbon disulfide or benzene.

Subst. 0.2100; 12.6 cc. N_2 (20° and 757.4 mm. over H_2O).
Calculated for $C_{11}H_{13}O_3N$: N, 6.77. Found: N, 6.80.
Subst 0.1469; 3.08 cc. standard NaOH: Theory, 3.10 cc.

By distilling the acid with excess of soda lime, a xylidine was obtained which gave an acetyl derivative melting at 98–9° (corr.). Jacobson[2] gives the melting point of the acetyl derivative of 4-amino-1,2-dimethylbenzene as 99°. As to the other possibilities, the acetyl derivative of *p*-xylidine melts at 180°, and that of *as-m*-xylidine at 120°.

Methyl ester.—Three grams of the acid were dissolved in excess of aqueous acid sodium carbonate solution and three grams of dimethyl sulfate added in small portions, warming after each addition. The ester separated in flocculent form and was crystallized from 50% alcohol until its melting point remained constant at 120° (corr.). Yield, 1.2 g. It forms colorless silky minute needles, easily soluble in ligroin, chloroform, carbon tetrachloride, ether, or benzene.

Subst. 0.1756; 9.6 cc. N_2 (19° and 766 mm over H_2O).
Calculated for $C_{12}H_{15}O_3N$: N, 6.33. Found: N, 6.31

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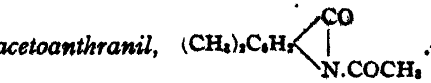
[1] Compare Kunckell, *Loc. cit.*

[2] *Ber.*, 17, 161 (1884).

3,4-Dimethylacetoanthranil,  $(CH_3)_2C_6H_2\left\langle\begin{array}{l}CO\\ |\\ N.COCH_3\end{array}\right.$.—Ten grams of the above acetamino acid were dissolved in 25 cc. of acetic anhydride, the solution boiled for 20 minutes and then concentrated. The crude product which separated was purified by repeated crystallization from acetic anhydride. It was thus obtained in nearly colorless minute crystals, melting at 263.5° (corr.), readily soluble in acetic anhydride, but practically insoluble in gasolene, ether or carbon tetrachloride. Yield, poor.

Subst. 0 2617; 16.6 cc. N_2 (18° and 763 mm. over H_2O).
Calculated for $C_{11}H_{11}O_2N$: N, 7 5. Found: N, 7.3.

This anthranil is very easily hydrated to the acid. On acting upon it with various amines, there seemed to be a general tendency for the condensation to stop at the intermediate amide stage, instead of continuing to the quinazolone; a difficulty which did not appear in the case of the anthranil from the dibasic acid.

2-Acetoamino-4,5-dimethylbenzamide, $(CH_3)_2C_6H_2(NHCOCH_3)CO.NH_2$.—Three grams of the above acetoanthranil were dissolved in small portions in an excess of concentrated ammonium hydroxide solution; then a little potassium hydroxide was added and the solution boiled for an hour. The clear solution was acidified with hydrochloric acid, and the precipitated amide purified by crystallization from 95% alcohol. It then formed microscopic cream-colored needles, which blacken but do not melt at 340°. The substance is very slightly soluble in ether, and practically insoluble in water, ligroin, carbon tetrachloride or benzene.

Subst. 0.2000; 23.2 cc. N_2 (18° and 762 mm. over H_2O).
Calculated for $C_{11}H_{14}O_2N_2$: N, 13.59. Found: N, 13 36.

2-Acetoamino-4,5-dimethylbenzmethylamide, $(CH_3)_2C_6H_2(NHCOCH_3).CO.NHCH_3$.—Three grams of the acetoanthranil were dissolved in 10 cc. of 33% aqueous methylamine solution, a few cc. of a 10% aqueous solution of potassium hydroxide were added, and the mixture boiled for a few minutes. On acidifying the cooled solution with formic acid, the amide separated instead of the expected quinazolone. Recrystallized from alcohol, this amide was obtained in microscopic colorless needles, which melt with decomposition at 320–2° (corr.), and are soluble in isoamyl alcohol or benzaldehyde, but practically insoluble in ligroin, carbon tetrachloride, ether, acetone or benzene.

Subst. 0.1425; 15.9 cc. N_2 (20° and 766.3 mm. over H_2O).
Calculated for $C_{12}H_{16}O_2N_2$: N, 12.73. Found: N, 12.79.

2,3,6,7-Tetramethyl-4-quinazolone, $CH_3.\dot{C} : N.C_6H_2(CH_3)_2.CO.\dot{N}.CH_3$.—Five grams of the acetoanthranil were dissolved in ten cc. of 30% aqueous methylamine solution, 5 cc. of concentrated (1 : 1) aqueous potassium hydroxide solution added, and the mixture boiled under a reflux condenser for two hours. The quinazolone separated gradually. Purified by crystallization from 50% alcohol, it formed colorless microscopic needles, melting at 210–2° (corr.), soluble in benzene, but practically insoluble in ether or ligroin. Yield, poor.

Subst. 0.1400; 17.4 cc. N_2 (19° and 756.3 mm. over H_2O).
Calculated for $C_{12}H_{14}ON_2$: N, 13.86. Found: N, 14.15.

2-Acetoamino-4,5-dimethylbenzanilide, $(CH_3)_2C_6H_2(NHCOCH_3)CONH\cdot C_6H_5$.—Four grams of the acetoanthranil were dissolved in ten cc. of aniline by warming, five cc. of 10% aqueous potassium hydroxide solution added, and the mixture boiled for 20 minutes, then cooled, acidified with acetic acid, and diluted. The white amorphous precipitate proved to be the anilide and not the quinazolone. Crystallized from dilute alcohol, it was obtained as a cream-colored microcrystalline solid, melting with decomposition at 307° (corr.); soluble in isoamyl alcohol or pyridine, but practically insoluble in ligroin, carbon tetrachloride, ether or benzene.

Subst. 0.1792; 15.4 cc. N_2 (18° and 760.9 mm. over H_2O).
Calculated for $C_{17}H_{18}O_2N_2$: N, 9.94. Found: N, 9.91.

2-Acetoamino-4,5-dimethylbenzhydrazide, $(CH_3)_2C_6H_2(NHCOCH_3)CONH-NH_2$.—Three grams of the acetoanthranil were dissolved in an excess of aqueous (50%) hydrazine hydrate solution, a little potassium hydroxide added and the solution warmed for a short time. When cold, it was acidified with formic acid and the yellow precipitate crystallized from 50% alcohol. Colorless microscopic needles resulted, melting with decomposition at 297° (corr.), moderately soluble in ether or pyridine, difficultly in ligroin or 50% alcohol, and practically insoluble in chloroform, carbon tetrachloride, acetone or benzene.

Subst. 0.1637; 26.4 cc. N_2 (18 5° and 762 mm. over H_2O).
Calculated for $C_{11}H_{15}O_2N_3$: N, 19.00. Found: N, 18.60.

3-Amino-2,6,7-trimethyl-4-quinazolone, $CH_3\overline{C:N.C_6H_2(CH_3)_2.CO.N}.NH_2$.—By boiling the above hydrazide with 10% potassium hydroxide solution and then acidifying with formic acid, this quinazolone was obtained. It crystallized from 50% alcohol in colorless microscopic needles, melting at 215° (uncorr.).

Subst. 0.0938; 17 cc. N_2 (18° and 759 mm. over H_2O).
Calculated for $C_{11}H_{13}ON_3$: N, 20.69. Found, N, 20.81.

4-Methyl-6-acetoaminoisophthalic Acid, $(HOOC)_2C_6H_2(CH_3)NH.COCH_3$.—Oxidation of acetopseudocumidide with potassium permanganate, in neutral or alkaline solution, yielded chiefly this dibasic acid, together with a smaller amount of the monobasic acetoaminodimethylbenzoic acid already described. The best results were secured by oxidizing with the permanganate at 95–100°, in presence of magnesium sulfate, but even then the best yield we could get of the dibasic acid was 25%.

1. A mixture of 20 grams of the acetopseudocumidide, 30 grams magnesium sulfate and five liters of water, was heated in a large evaporating dish at 95–100°, and a solution of 80 grams of potassium permanganate run in slowly, stirring mechanically. The oxidation was completed in three hours. The hot solution was filtered, the filtrate acidified with hydrochloric acid, and the flocculent precipitate crystallized from 50% acetic acid. Colorless microscopic needles were thus obtained, which turned yellow and shrunk at 250–5°, and melted at 278–80° (corr.) with evolution of carbon dioxide and decomposition. Yield, 6 g.

2. Oxidations were also carried out in presence of potassium chloride instead of magnesium sulfate. Eighty grams of potassium chloride were dissolved in two and a half liters of water, four grams of the cumidide added, the solution heated to boiling, stirred mechanically, and a solution of 22 grams of potassium permanganate gradually dropped in. The oxidation was completed in two hours, but on filtering and acidifying the filtrate with hydrochloric acid, nothing precipitated even on long standing.

3. In this experiment the conditions were exactly the same as in the last, except that the oxidation was conducted at 62–4°. After ten hours the oxidation was still uncompleted, so about a third of the mixture was removed, the excess of permanganate reduced by alcohol, the solution filtered and acidified with hydrochloric acid. The precipitate which formed softened at 267–70°, but did not melt completely at 300°, and was not separated in sufficient amount for identification.

The remaining two-thirds of the original mixture were heated five and a half hours longer at 80° with constant stirring. Half of this was then taken, the excess of permanganate reduced by adding alcohol, the solution filtered and acidified with hydrochloric acid. The amorphous precipitate resulting proved to be a mixture of the mono- and dibasic acids.

The final third of the original mixture, after having stood for 24 hours longer at laboratory temperature, was found to have become decolorized. On filtering and acidifying the filtrate, a beautiful crystalline precipitate separated gradually, which proved to be the tribasic acid and is described beyond.

4. In another experiment, the oxidation was conducted at 40–50° for three days, with constant stirring, and gave only mono- and dibasic acids.

The dibasic acid is easily freed from the monobasic by crystallization from water or from 50% acetic acid, in both of which the monobasic acid is much more soluble, as already mentioned in connection with the latter acid.

The pure acid forms colorless microscopic needles, which shrink somewhat at about 250–5°, and melt with decomposition at about 278–80° (corr.), as noted above. It is easily soluble in alcohol, moderately in acetone, and practically insoluble in ligroin, chloroform, ether or benzene.

Calculated for $C_{11}H_{11}O_5N$: C, 55.66; H, 4.68; N, 5.92. Found: C, 55.36, 55.51; H, 4.83, 4.83; N, 6.28, 6.23.

Distilled with excess of soda lime, the acid yielded a toluidine whose acetyl derivative melted at 64.8° (corr.). A sample of aceto-*m*-toluidide, prepared from some Kahlbaum *m*-toluidine, melted at 65.2° (corr.). Aceto-*o*-toluidide melts at 110° and aceto-*p*-toluidide at 153°. The methyl groups of the acetopseudocumidide which have been oxidized by the above treatment are therefore those at positions 2 and 4, thus giving an isophthalic acid.

Dimethyl Ester.—Four grams of the acid were dissolved in a solution of five grams acid sodium carbonate, causing a marked lowering of temperature. The solution was warmed gently, about six grams of dimethyl sulfate added gradually, and the mixture left over night. The ester separated as a flocculent amorphous solid. It was filtered out and crystallized from 50% alcohol. Yield, 3.3 g. The pure ester forms colorless silky hairs; melting at 138° (corr.); easily soluble in chloroform, ether, carbon, disulfide, acetone, ethyl acetate, benzene or pyridine; moderately soluble in ligroin; and practically insoluble in water.

Subst 0.2513 CO_2, 0.5417, H_2O, 0.1278.
Calculated for $C_{13}H_{15}O_5N$: C 58.84; H, 5.70. Found: C, 58.75; H, 5.65

This compound was also prepared by acetylating the aminomethylisophthalic ester.

Diethyl Ester.—Four grams of the aminomethylisophthalic ester were dissolved in excess of acetic anhydride, the solution evaporated to dryness and the final traces of the anhydride removed by leaving the material in a vacuum desiccator over solid potassium hydroxide. The crude product crystallized from 50% alcohol in colorless minute needles, melting at 116.5° (corr.); easily soluble in chloroform, ether, acetone, carbon disulfide, ethyl acetate, benzene or pyridine; moderately soluble in ligroin; and but very slightly soluble in hot water. Yield, 4 g.

Subst. 0.3001; 12.7 cc. N_2 (18° and 760.2 mm. over H_2O).
Calculated for $C_{15}H_{19}O_5N$ N, 4.78. Found N, 4.83

4-Methyl-6-aminoisophthalic Acid, $(HOOC)_2C_6H_2(CH_3)NH_2$.—This acid was secured by the hydrolysis of the above acetoamino acid. The hydrolysis was effected more satisfactorily by acid than by alkali.

Four grams of the acetoamino acid were added gradually, with stirring, to a hot solution of 15 cc. of dilute sulfuric acid (9 cc. concentrated acid and 6 cc. water), the clear solution heated quickly to boiling, boiled for about a minute, and then poured into cold water,[1] the amino acid separating as a flocculent precipitate. It crystallized from water in colorless long needles, melting at 305–8° (corr.), which dissolve in alcohol or acetic

[1] Compare Mayer, *Ber.*, 44, 2300 (1911).

acid, but are practically insoluble in ligroin, chloroform, ether, ethyl acetate or benzene.

Subst. 0.2132; 14.2 cc. N_2 (22° and 762 mm. over H_2O).
Calculated for $C_9H_9O_4N$: N, 7.17. Found: N, 7.11.

By the action of acetic anhydride, the acetoamino acid is reproduced.

Hydrochloride.—Three grams of the acid were boiled under a reflux condenser with 10 cc. of concentrated hydrochloric acid. After boiling four hours, a clear solution was obtained, and, on cooling, the entire contents of the flask set to a mass of needle crystals. These were recrystallized from concentrated hydrochloric acid and dried over solid potassium hydroxide. They are easily soluble in water, but very difficultly soluble in cold concentrated hydrochloric acid, and melt with decomposition at 196–7° (corr.). Yield, 2.8 g.

Subst. 0.1416; AgCl, 0.0870.
Calculated for $C_9H_{10}O_4NCl$: Cl, 15.3. Found: Cl, 15.1.

Dimethyl ester.—The acetoamino acid was used for the preparation of this ester.

Five grams of the acetamino acid were suspended in 200 cc. of absolute methyl alcohol, the mixture heated under a reflux condenser and saturated with dry hydrogen chloride. The acetoamino acid dissolved gradually, forming a light yellow solution, and the odor of methyl acetate was noted. After passing hydrogen chloride through it for two hours, the hot solution, which had become a deep red, was allowed to cool. The hydrochloride of the ester separated in crystals. These were filtered out and a second crop obtained by concentration of the mother liquor. The amino ester was liberated from this hydrochloride by treatment with sodium carbonate solution in slight excess, and then crystallized from 50% alcohol. Fine colorless silky hairs resulted, melting at 150 °(corr.); easily soluble in chloroform, ether, ethyl acetate, carbon disulfide, benzene or pyridine; slightly soluble in ligroin; and insoluble in water.

Subst. 0.1620; 8.90 cc. N_2 (19° and 760.4 mm. over H_2O).
Calculated for $C_{11}H_{13}O_4N$: N, 6.28. Found: N, 6.29.

After precipitating the free ester from its hydrochloride by the action of excess of sodium carbonate solution, this carbonate mother liquor was acidified and a white flocculent precipitate obtained. Crystallized from dilute alcohol, it formed colorless minute needles, melting at 217° (uncorr.); soluble in aqueous alkalies. It is perhaps an acid ester. Not enough of it was recovered to investigate further.

Diethyl Ester.—This was prepared in an entirely analogous manner, using absolute ethyl alcohol instead of methyl. It crystallized from dilute alcohol in straw-yellow glassy needles, melting at 103.5° (corr.); easily soluble in ligroin, chloroform, ether, ethyl acetate, carbon disulfide, benzene or pyridine; insoluble in water.

Subst. 0.2669; CO_2, 0.6795; H_2O, 0.1866.
Calculated for $C_{13}H_{17}O_4N$: C, 62.15; H, 6.82. Found: C, 62.48; H, 6.98.

Acetoanthranil of 4-Methyl-6-amino Isophthalic Acid, $HOOC(CH_3)\overline{C_6H_2.CO.N}.COCH_3$.—Twenty-five grams of the acetoamino acid were dissolved in 40 cc. of acetic anhydride, the solution heated just below its boiling point until its volume was reduced to 20 cc., and then allowed to cool. The acetoanthranil separated in clusters of microscopic yellowish needles, which were recrystallized repeatedly from acetic anhydride, washed with dry benzene and carefully dried. As thus purified, it melts at 285–6° (corr.); it is difficultly soluble in chloroform or ethyl acetate; and apparently insoluble in ligroin, ether, benzene or toluene. Moisture rapidly hydrates it, regenerating the acetoamino acid.

Subst 0.1857; 10.3 cc. N_2 (24° and 769 mm. over H_2O).
Calculated for $C_{11}H_9O_4N$: N, 6.38. Found: N, 6.30.

It can be prepared in similar manner from the amino acid itself.

2-Methyl-4-acetoamino-5-carbaminobenzoic Acid, $HOOC(CH_3)C_6H_2(NH.CO.CH_3)CONH_2$.—Four grams of the above acetoanthranil were added in small portions to 12 cc. of concentrated ammonium hydroxide solution. The reaction was vigorous. the anthranil dissolving to a clear solution. This solution was boiled for ten minutes, then cooled, filtered, and acidified with hydrochloric acid. The precipitated amide separated from 60% alcohol in nearly colorless microscopic short glassy crystals, which melt to a dark liquid at 303–5° (corr.), and are soluble in acetone, but practically insoluble in ligroin, chloroform, ether or benzene.

Subst. 0.1823; 19.0 cc. N_2 (19° and 768.3 mm. over H_2O).
Calculated for $C_{11}H_{12}O_4N_2$: N, 11.87. Found: N, 11.98

2,7-Dimethyl-4-quinazolone-6-carboxylic Acid, $CH_3.\overline{C : N.C_6H_2(CH_3)(COOH).CO.NH}$.—The acetoanthranil was dissolved in concentrated ammonium hydroxide solution, some potassium hydroxide was added, the solution boiled about an hour, cooled, and acidified with hydrochloric acid. The precipitated quinazolone was extracted with boiling alcohol, to remove any amide, then dissolved in ammonium hydroxide solution, reprecipitated by hydrochloric acid, washed and dried. It is apparently insoluble in water, ligroin, alcohol, ether, acetone or benzene; at 340° (corr.), it chars without melting.

Subst. 0.1834; 20.95 cc. N_2 (21° and 762.6 mm. over H_2O).
Calculated for $C_{11}H_{10}O_3N_2$: N, 12.85. Found: N, 12.98

2,3,7-Trimethyl-4-quinazolone-6-carboxylic Acid, $CH_3.\overline{C : N.C_6H_2(CH_3)(COOH).CO.N}.CH_3$.—Three grams of the acetoanthranil were dissolved in eight cc. of 33% aqueous methylamine solution, a little potassium hydroxide added, the solution boiled for ten minutes and then neutralized with acetic acid. On cooling, the contents of the flask set to a crystalline mass of the quinazolone. These crystals were separated, washed with hot water, and recrystallized from 95% alcohol, until they showed a constant melting point of 299.5° (corr.). Yield, 1.2 g. The purified compound forms colorless microscopic crystals, difficultly soluble or insoluble in water, ligroin, ether, ethyl acetate or benzene. It is easily soluble in aqueous alkalies, and reprecipitates when these solutions are acidified.

Subst. 0.1501; 16.1 cc. N_2 (20° and 761 mm. over H_2O).
Calculated for $C_{12}H_{12}O_3N_2$: N, 12.07. Found: N, 12.22.

2,7-Dimethyl-3-ethyl-4-quinazolone-6-carboxylic Acid, $CH_3.\overline{C : N.C_6H_2(CH_3)(COOH)CO.N}.C_2H_5$, prepared in a similar manner, crystallized from 30% alcohol in colorless silky needles, melting sharply (with decomposition) at 250.8° (uncorr.), and showing much the same solubilities as the above trimethyl compound.

Subst. 0.2170; 21.8 cc. N_2 (22° and 758 mm. over H_2O).
Calculated for $C_{13}H_{14}O_3N_2$: N, 11.38. Found: N, 11.30.

2,7-Dimethyl-3-phenyl-4-quinazolone-6-carboxylic Acid.—Four grams of the acetoanthranil were dissolved in 10 cc. of aniline, the solution boiled ten minutes, cooled, and neutralized with dilute hydrochloric acid. The precipitated quinazolone was crystallized from 80% alcohol, from which it separated in minute pale yellow needles, melting at 300–1° (corr.), practically insoluble in ether or benzene.

Subst. 0.1578; 13.2 cc. N_2 (23° and 765.7 mm. over H_2O).
Calculated for $C_{17}H_{14}O_3N_2$: N, 9.53. Found: N, 9.48.

2,7-Dimethyl-3-amino-4-quinazolone-6-carboxylic Acid.—Three grams of the acetoanthranil were added in small portions to an excess of aqueous hydrazine hydrate solution (50%). The anthranil dissolved with evolution of heat. Dilute potassium hydroxide solution was added, the liquid heated to boiling for a short time, left over night, and then acidified with acetic acid. The quinazolone separated gradually in minute silky needles, which were recrystallized from dilute alcohol. Yield, 2.8 g. It melts with decomposition at 306° (corr.), is difficultly soluble in acetone and apparently insoluble in ligroin, chloroform, ether, carbon disulfide or benzene.

Subst. 0.2521; 40.4 cc. N_2 (20.5° and 765.6 mm. over H_2O).
Calculated for $C_{11}H_{11}O_3N_3$: N, 17.95. Found: N, 18.12.

Acetyl Derivative.—Three grams of the above aminoquinazolone were dissolved in 12 cc. of acetic anhydride, the solution evaporated to small volume and then placed in a vacuum desiccator over solid potassium hydroxide. The crude product was crystallized first from dilute acetic acid and then from alcohol. Transparent glassy minute plates were obtained, melting at 220° (uncorr.); soluble in ethyl acetate, but apparently insoluble in ligroin, ether, carbon disulfide or benzene.

Subst. 0.1475; 19 cc. N_2 (19° and 762 mm. over H_2O)
Calculated for $C_{13}H_{13}O_4N_3$: N, 15.27. Found: N, 14 8.

Evaporation of the amino quinazolone with glacial formic acid failed to yield any formyl derivative.

Benzal derivative.—When a mixture of three grams of the amino quinazolone with excess of benzaldehyde was heated to boiling, water was driven out and, on cooling, needles separated. These were recrystallized from a mixture of benzaldehyde and alcohol (1 : 4), as good crystals could not be secured from other solvents tried. The minute straw-colored needles so obtained were washed with ether, to remove benzaldehyde, and dried. They are soluble in water, ligroin, alcohol or acetic acid, but practically insoluble in ether. At 237.5° (corr.), they melt to a clear liquid which decomposes at 278° (corr.). The substance decolorizes a bromine solution.

Subst. 0.2032; 23 2 cc. N_2 (22° and 760.7 mm. over H_2O).
Calculated for $C_{18}H_{16}O_3N_3$: N, 13.09. Found: N, 13 00.

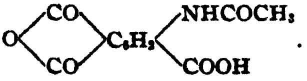
Dimethyl 4-Methyl-6-phenyluraminoisophthalate, $(CH_3OOC)_2C_6H_2(CH_3).NH.CO.NHC_6H_5$.—Four grams (one mole) of dimethylmethylaminoisophthalate were dissolved in 60 cc. of carefully dried benzene, 2.1 grams (one mole) of phenyl isocyanate added, the solution boiled for two hours under a reflux condenser, then concentrated to half its original volume and allowed to cool. The crystals which separated were washed with dry benzene, to remove any unchanged isocyanate, and recrystallized from 95% alcohol. Rosettes of colorless microscopic needles resulted, melting at 192.5° (corr.); easily soluble in alcohol, acetone or pyridine, moderately in chloroform or benzene, difficultly in ether, and apparently insoluble in carbon tetrachloride or carbon disulfide. It was not hydrolyzed by boiling for three hours with dilute hydrochloric acid.

Subst. 0.2509; 18.40 cc. N_2 (21° and 757 mm. over H_2O).
Calculated for $C_{18}H_{18}O_5N_2$: N, 8.19. Found: N, 8.23.

Diethyl Ester.—Prepared in a similar manner, this ester crystallized from 95% alcohol in colorless microscopic needles, melting at 177–8° (corr.); easily soluble in alcohol, chloroform, ether, acetone, benzene or pyridine; slightly soluble in ligroin, carbon tetrachloride or carbon disulfide. Yield, 2.6 g. from 3 g. of the initial compound.

Subst. 0.2005; 13.5 cc. N_2 (20° and 762 mm. over H_2O).
Calculated for $C_{20}H_{22}O_5N_2$: N, 7.57. Found: N, 7.66.

Anhydride of 5-Acetamino-1,2,4-benzenetricarboxylic Acid,



$$O\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3\left\langle\begin{matrix}NHCOCH_3\\COOH\end{matrix}\right. .$$

—In describing the preparation of the acetoaminomethylisophthalic acid by oxidation of acetopseudocumidide, it is there noted that in one case (No. 3), when the oxidation was conducted at moderate temperature (62–4°), some of this tribasic acid was isolated. It crystallized from water in regular glassy prisms, which fell to powder on drying. This powder melts with decomposition at 240–2° (corr.), and is soluble in alcohol, and apparently insoluble in ether.

Subst. 0.2046; 9.79 cc. N_2 (16° and 772 mm. over H_2O).

Calculated for $C_{11}H_7O_6N$: N, 5.63. Found: N, 5.64.

Subst. 0.1989; 9.80 cc. standard KOH solution. Theory for anhydride of the tribasic acid, 9.80 cc.

The glassy crystals first obtained by crystallization from water were, therefore, probably the acid itself. Unfortunately, the amount of substance isolated was too small for further study, and experiments to secure more of it have so far proven fruitless. An oxidation carried out at laboratory temperature, and lasting 32 days in all, yielded only the mono- and dibasic acids. Attempts to oxidize the dibasic acid in various ways also proved failures, the acid being invariably either unchanged or else wholly destroyed with evolution of carbon dioxide.

3. Summary.

1. A number of new derivatives of 2,4,5,7-tetramethylbenzimidazole are described.

2. Propionopseudocumidide was prepared, and from it the benzimidazole and other new derivatives.

3. Oxidation of acetopseudocumidide gives mono- and dibasic acids. Only in one experiment was a small amount of tribasic acid isolated.

4. The structure of the acids so produced indicates that the methyl group in position 4 is first oxidized, then that at 2.

5. As both the mono- and the dibasic acid so obtained are of anthranilic type, they yield acyl anthranils and 4-quinazolones by the usual methods.

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[CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION.]

UTILIZATION OF THE PROTEINS OF COTTON SEED BY MAN.

BY J. B. RATHER.[1]

Received January 1, 1914.

Cotton seed meal has been used, to some extent, as a human food, for a number of years in the South. In Texas, at least, it is claimed to be used both by those who are too poor to buy sufficient meat, and by those who use it by preference, mixing it with wheat flour. Since cotton seed meal contains more than twice as much protein as meat, and since it can be prepared in palatable form, and is enormously cheaper than animal foods, the utilization value of the proteins by man is of practical as well as theoretical importance.

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[1] Under the general direction of G. S. Fraps, Chemist. Abstracted by the author from *Bulletin* 163 of the Texas Experiment Station.

We have been unable to find in the literature any mention of the digestibility of cotton seed meal by man. Mendel and Fine[1] reported the results of experiments on dogs with cotton seed flour, which is prime cotton seed meal, finely ground and freed, as much as possible, from hulls. They found that the proteins were utilized on an average 71.6%, as compared with 94% for fresh meat.

Experimental.

In the experiments here reported, the cotton seed meal was fed in a simple mixed diet of milk, butter, and bread made of corn meal and the cotton seed meal, or flour, to be tested. Three men were used in one trial and two in the others. In order to get a direct comparison with meat, two trials were made with chicken loaf, a canned meat product. While this substance apparently did not consist entirely of meat, the average utilization was practically the same as Atwater's average for animal proteins.

The cotton seed meal was ordinary commercial meal. It was sifted through a 20-mesh sieve before use. The cotton seed flour was made from prime meal by a roller mill process, was practically free from hulls, and was very finely ground. The sifted cotton seed meal contained 46.33% protein, and the flour contained 50.16% protein. The cotton seed meal-corn meal mixture used in the ration, contained corn meal, salt, and about 20% cotton seed meal or flour. The bread was made up with water.

The digestion trials were conducted in the usual manner. They lasted for two days each, charcoal being used as a marker. The amount of protein in the water-free bread, less the amount of corn meal protein in the water-free meal mixture, was taken as the amount of cotton seed protein fed. The following utilization values for proteins were assumed in the calculation: milk 97%, and corn meal 85%.

The results are summarized in the table on following page.

The utilization value of the protein of cotton seed meal varied from 74.7 to 80.2%, and averaged 77.6%. That of the cotton seed flour varied from 79.2% to 79.7%, and averaged 79.5%. We do not attach any significance to the difference of these averages. The average of the values of both the meal and flour is 78.6%. The protein of cotton seed meal and cotton seed flour seem to be equally available to man. The average utilization of the meat proteins was 96.6%. Since the proteins of cereals are utilized 85% and those of legumes 78%, cotton seed proteins are utilized equally as well as those of legumes, nine-tenths as well as those of cereals, and eight-tenths as well as those of meat.

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[1] *J. Biol. Chem.*, 11, 1.

Utilization of the Proteins of Cotton Seed by Man.

	Proteins, Grams.									
	Milk.	Corn meal.	Meat.	Cotton seed meal.	Total eaten.	Excreted.	Utilized.	Utilized from milk and corn.	Utilized from food tested.	Utilization value, Per cent.
Cotton seed meal, man 1	132.4	10.6	...	25.3	168.3	10.5	157.8	137.5	20.3	80.2
Cotton seed meal, man 2	142.6	38.6	...	50.3	221.5	22.5	199.0	161.4	37.6	74.7
Cotton seed meal, man 3	123.6	37.0	...	48.3	208.9	23.5	185.4	151.3	34.1	77.9
Cotton seed meal, average.										77.6
Cotton seed flour, man 1	108.4	35.5	..	47.2	191 1	19.5	171 6	134.0	37.6	79.7
Cotton seed flour, man 2	122 0	41.4	...	59 6	223 4	22.3	201.1	153.9	47.2	79.2
Cotton seed flour, average............... .										79.5
Meat, man 1	96.3	23.5	101.5	.	221 3	7.1	214.2	113.4	100.8	99.3
Meat, man 2..	85 0	35.8	95 0	..	215 8	13.7	202 1	112.9	89.2	93.9
Meat, average....										96.6

These results are higher than those obtained by Mendel and Fine with dogs, relatively (in comparison with meat) about 5%, and actually, about 7%.

It is generally considered that man's utilization of concentrated foods is equal to ruminants, but it is interesting to note that ruminants utilize 88% of the proteins of cottonseed, whereas man utilizes only 78%.

Summary.

The utilization values of the proteins of cotton seed meal and flour are the same and average 78.6%. Experiments with meat, on the same men, showed that 96.6% of the proteins was utilized.

Cotton seed proteins are utilized by man equally as well as those of legumes, nine-tenths as well as those of cereals, and eight-tenths as well as those of meat.

College Station, Texas.

[Contribution from the Harriman Research Laboratory, Roosevelt Hospital, New York City.]

ON THE ACTION OF ACIDS UPON FRUCTOSE AND GLUCOSE.

By M. M. Harrison.

Received January 15, 1914.

1. Introductory.

It has long been known that the two hexoses of invert sugar are more or less rapidly acted upon by acids. The effect is of no little importance in studies of sugar hydrolysis, for the velocity coefficient of the reaction can only be calculated on the basis of the rotation observed when inversion is complete. It seemed interesting, therefore, to investigate carefully, to just what extent and under what physico-chemical conditions the composition, and with it the rotatory power, of an invert sugar solution is appreciably modified by the action of such acids as are likely to be employed as catalyzers of sugar hydrolysis. Incidentally, it appeared desirable to reinvestigate the nature of the decomposition itself by physico-chemical methods, with a view to uncovering something of the mechanism of that decomposition. The effect of two acids was studied, *viz.*, hydrochloric and formic, the former as a representative of the strong mineral acids, the latter as a representative of the weaker organic acids, and also because it is the catalyzer employed in a reinvestigation of the mechanism of sugar hydrolysis at present carried on at Clark University. The effect of these acids was studied first on fructose alone and then on glucose alone. The physico-chemical changes attending the decomposition could be more conveniently followed in presence of the stronger than of the weaker acid, and consequently most of the experiments recorded below were carried out with hydrochloric acid only.

2. Decomposition of Fructose by Acids at 60°.

The decomposition of fructose by acids has been studied by a number of authors under a variety of conditions, the strength of the acid, for instance, varying from 0.01% to perhaps 40% in the case of hydrochloric acid. Other acids, too, including sulfuric, nitric, phosphoric and oxalic, have been employed in various degrees of concentration. The solutions studied have also been considerably varied in sugar concentration and the temperatures at which the action was allowed to take place. The present study was carried out, for the most part, at 60°, a temperature which permitted studying the kinetics of the change with more or less precision. A normality of about 0.7 of the hydrochloric acid was found, after some preliminary experimenting, to serve my purposes best.

The solutions were prepared by dissolving weighed amounts of Kahlbaum's fructose (not re-dried) in water, keeping the solution for a time at 60°, then adding the required amount of acid, making at once the necessary initial observation, then gradually observing the progress of the reaction in time. The thermostat in which the solutions were kept was maintained at 60 ± 0.05°. The polarimetric measurements were made with a Schmidt and Haensch saccharimeter, an incandescent Welsbach gas lamp, with a bichromate solution ray filter, being used as a source of light. The one decimeter jacketed Landolt observation tube was kept constantly at 35°, the work being carried on in midsummer. For an observation, a sample was pipetted out at a noted time, thoroughly cooled, and usually treated cold with boneblack, which diminished coloration and permitted of more precise polarimetric readings. A special experiment showed that the boneblack treatment did not affect the rotation of the solutions.

The increasing acidity of the solution, which is due, as will be seen, to the appearance of formic and levulinic acids, was also measured by pipetting out sufficient samples at noted intervals of time and titrating with 0.05-normal barium hydroxide and phenolphthalein. The titrations were carried out in a closed vessel, and the solution was covered with a layer of purified toluene, to avoid any disturbing effect from atmospheric carbon dioxide—a practice which has been in use in the Clark University laboratories for some years past. A weighing buret was used throughout.

Finally, the increasing coloration of the solution, which is due to the formation of humin substances, was measured with the aid of an excellent Duboscq colorimeter.

The results of these measurements are recorded numerically in Tables I–IV and graphically in Figs. 1–3.

Conrad and Guthzeit[1] found, as far back as 1886, that fructose is entirely decomposed into levulinic acid, formic acid, and humin by heating with 5 or 10% hydrochloric acid. A few years later, Wohl,[2] working with a 92.3% solution of fructose containing about 0.01% hydrochloric acid, kept at 100° for one hour, was able to separate an extremely hygroscopic "dextrin-like substance," which he named *levulosin* and which he supposed to be a mixture of dehydration products of fructose. Its rotatory power he found to be about one-half that of fructose. He further states that in dilute solution levulosin is changed back to fructose by 0.6-normal hydrochloric acid. Still later, Kiermayer[3] found hydroxymethylfurfural, $C_4H_2O(CH_2OH)CHO$, as a constant intermediate product in the decomposition of fructose. This author believes that the mechanism of the reaction consists in the direct transformation of fructose into humin and hydroxymethylfurfural, the latter then gradually changing into formic and levulinic acids.

One of the first questions that suggested themselves in the present study was, whether Wohl's levulosin is formed, not only under the particular conditions of his experiments, but also under other conditions, including those chosen by myself. A further question that arose was, whether humin and hydroxymethylfurfural were formed directly from fructose, or, by a secondary reaction, from one of the intermediate products. Finally, it seemed desirable to attempt to learn something of the order of the reaction, to see whether each single molecule of fructose is attacked by itself or whether two or more molecules take part in the reaction together.

[1] *Ber.*, 19, 2569 (1886).

[2] *Ibid.*, 23, 2084 (1890).

[3] *Chem.-Ztg.*, 19, 1004 (1895).

To establish the formation of levulosin under the conditions chosen, an attempt was made to actually separate this substance from one of the solutions. A solution of Schering's fructose in 0.7-normal hydrochloric acid, having a rotation of —28.2° in a 5 cm. tube, was heated at 60° for 84 hours; the precipitated humin was filtered off, and the filtrate neutralized with silver hydroxide. After removing the silver chloride formed and decomposing the soluble silver salts of the organic acids with hydrogen sulfide, the solution was decolorized with boneblack and the water distilled off at 30° *in vacuo*. When dry, the cream-colored residue was dissolved in asbolute alcohol and partly precipitated by adding 25%, by volume, of absolute ether. The precipitate, a waxy snow-white solid, was next washed with absolute ether and dried over phosphorus pentoxide in a vacuum desiccator. The product was extremely hygroscopic and formed a golden yellow solution in water. An analysis of the substance gave the following results:

	Found.		Theory for $C_6H_{10}O_5$	Theory for $C_6H_{12}O_6$
	I. Per cent	II Per cent	Per cent	Per cent
C	41 9	41 7	44 4	39 9
H	6 66	6 67	6 2	6 7
O	51 4	51 6	49 4	53 4

These results point to the product being a mixture of fructose, $C_6H_{12}O_6$, and levulosin, which apparently has the formula $C_6H_{10}O_5$, the mixture under consideration containing about 57% of fructose and some 43% of levulosin. A molecular weight determination by the cryoscopic method was accordingly expected to give a figure slightly above 170. The result actually obtained was somewhat low, about 162; yet it indicates clearly enough the molecular magnitude of levulosin. The nature of the product was further indicated by a determination of its rotatory power. If it is a mixture of fructose and levulosin, containing somewhat more of the former than of the latter, its rotation should be intermediate between that of the two pure substances and somewhat nearer to that of fructose. (The rotatory power of levulosin is, according to Wohl, only about one-half that of fructose.) Measurement fully bore out this conclusion. A 2.32% soln. of the product gave, in a 20 cm. tube at 35°, a rotation of —8.2°, and a 4.24% solution, under similar conditions, gave a rotation of —14.8°. These figures would indicate the product to contain roughly about 60% of fructose and 40% of levulosin. When warmed with acid of the same strength (0.7-normal) as used in its formation, the product underwent a readily measurable change. The solution being made more dilute with respect to the product, that is, the concentration of the water being made greater than in the solution in which it had been formed, the result was an increase in the proportion of fructose present, as clearly indicated by the increase of the negative rotation.

It seems plain, therefore, that levulosin is a dehydration product of fructose and that it is formed from the latter and changed back into it by a reversible reaction.

As has been mentioned above, the decomposition products of fructose include, beside levulosin: hydroxymethylfurfural, formic and levulinic acids, and humin. The question now presented itself, are these substances formed, together with levulosin, directly from fructose itself, or are they decomposition products of levulosin? If the latter is the case, as seems more probable *a priori*, then one would expect, in the first place, the decrease of the negative rotation to run a peculiar course. At first, namely, the fall in rotation should be rapid, the amount of levulosin being formed which is necessary to hold equilibrium to the fructose in the reversible reaction. Then the fall in rotation should become strikingly slower, corresponding to the undoubtedly slow decomposition of levulosin into humin and the other substances mentioned. This is exactly what was observed, as shown by Curve A in Fig. 1, which represents graphically the data of Table I.

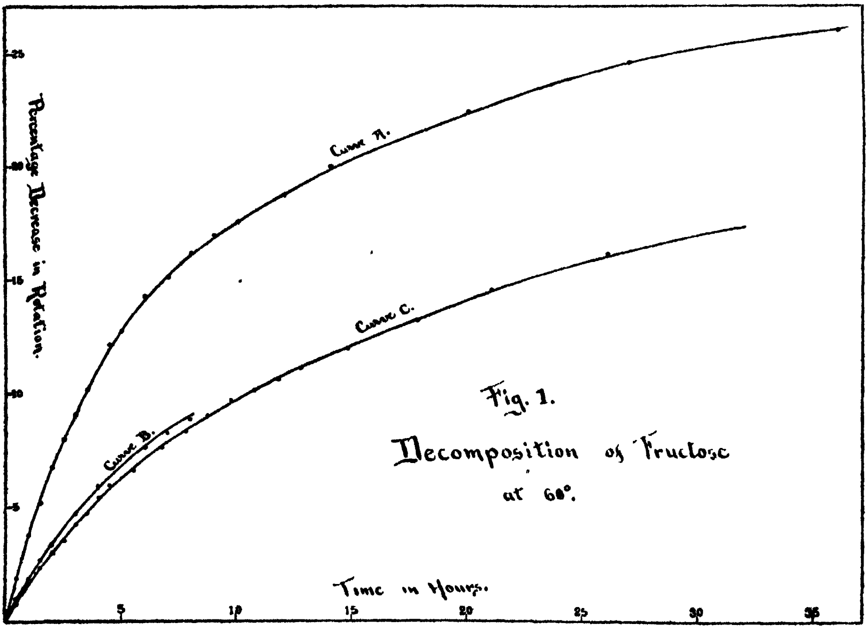

Fig. 1.
Decomposition of Fructose at 60°.

Some additional experiments indicated that, while under these conditions the solution loses about a fifth of its original rotation in a very few hours, loss of the remaining rotation would take at least two months.

That the formic and levulinic acids found among the final decomposition products of fructose originate, not from the sugar itself, but from an intermediate product, was more directly shown by the peculiar course of

TABLE I.—300 CC. OF THE SOLUTION CONTAINED 100 g. FRUCTOSE AND 231 g. WATER AND WAS 0.7453-NORMAL WITH RESPECT TO HYDROCHLORIC ACID.

Time in hours.	Rotation.	Per cent. change.	Time in hours.	Rotation.	Per cent. change.
0.0	—84.5°	0	6.0	—72.45°	14.3
0.5	—82.9	1.9	7.0	—71.55	15.3
1.0	—81.3	3.8	8.0	—70.8	16.2
1.5	—79.9	5.4	9.0	—70.15	17.0
2.0	—78.75	6.8	10.0	—69.6	17.6
2.5	—77.7	8.0	12.0	—68.55	18.8
3.0	—76.75	9.1	14.0	—67.6	20.0
3.5	—75.85	10.2	20.0	—65.55	22.4
4.5	—74.3	12.1	27.0	—63.7	24.6
5.0	—73.65	12.8	36.0	—62.5	26.0

the gradual increase of acidity. If, namely, the acids were formed from fructose directly, their rate of formation would decrease with the sugar. Plotted graphically, the gradual increase of acidity would appear in the form of a curve concave downward toward the time-axis. If, on the contrary, the acids were slowly produced from a more rapidly forming intermediate product, then the curve of increasing acidity should exhibit two phenomena: it should be concave upward during a first considerable stretch, and at its origin, *i. e.*, at the point $t = 0$, its direction should be coincident with that of the time axis itself. The upward concavity of the curve would indicate an increasing rate of acid formation due to accumulation of the intermediate product from which the acids are formed. The tangency between the curve and the time axis at the very beginning would indicate that before any intermediate product has appeared and there is nothing but pure fructose present, the rate of acid formation is zero. *Fig. 2, representing the actual measurements, exhibits both of these phenomena.* The measurements are reproduced numerically in Table II.

TABLE II.—600 CC. OF THE SOLUTION CONTAINED 100 g. FRUCTOSE AND 526 g. WATER, AND WAS 0.7453-NORMAL WITH RESPECT TO HYDROCHLORIC ACID.

Time in hours.	Percentage increase of acidity.	Time in hours.	Percentage increase of acidity.
0	0.00	14.75	0.72
0.5	0.00	17.75	0.87
1.0	0.00	21.00	1.2
1.5	0.01	26.00	1.8
2.0	0.04	32.00	2.4
2.5	0.10	42.00	3.3
3.5	0.15	57.00	5.4
4.0	0.15	82.00	9.5
4.5	0.16	97.00	12.8
5.5	0.17	120.00	15.5
6.75	0.19	144.00	17.9
11.75	0.58	168.00	20.4
12.75	0.60	192.00	24.4
		216.00	26.4

To express the increase in acidity in percentage form, I determined the total acid formed when decomposition was complete, which was attained after heating the solution at 75° for eighteen days. It appeared that

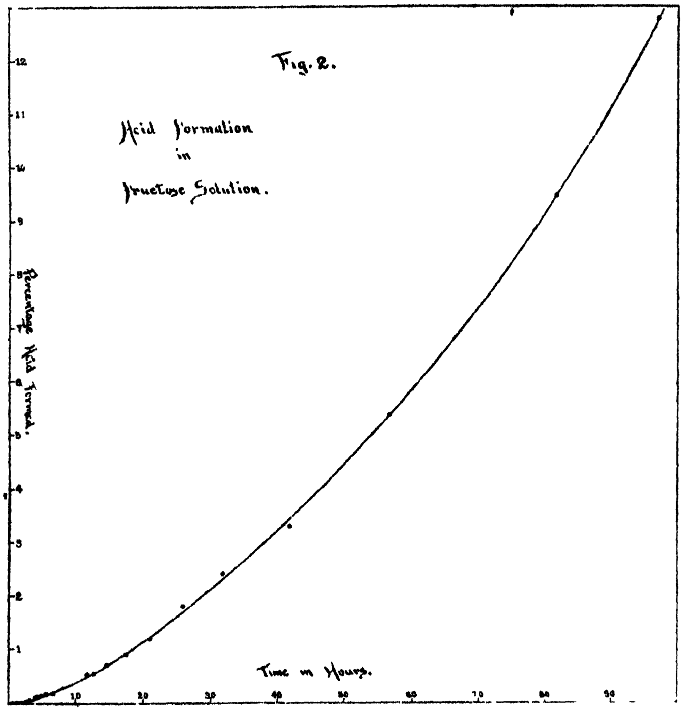

Fig. 2.

Acid Formation in Fructose Solution.

69.7% of the original fructose was finally turned into acids, the remaining 30% being presumably changed into humin.[1] The final normality of the organic acids formed was 1.289.

The rate of humin formation was studied next. The only method from which reasonable accuracy might be expected was the colorimetric method. The color intensity of the investigated solution, just before humin began settling out of it, was arbitrarily taken as unity, and the coloration gradually increasing to that point when expressed in fractions of that unit. The results are shown graphically by Fig. 3.

As in the case of acid formation, the curve of increase of color intensity is concave upward. This shows that, like formic and levulinic acids, humin is produced mainly from an intermediate product. If none were produced from fructose directly, the curve would also be tangent with the time axis at the origin, as in the case of the curve of acid formation.

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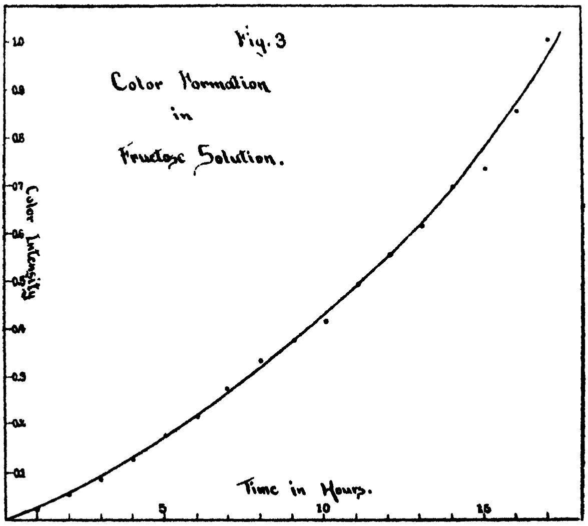
[1] One of the sets of data given by Conrad and Guthzeit (*loc. cit.*) indicates that under their working conditions about the same percentages of the fructose are changed into acids and humin, respectively.

This tangency is not indicated by the figure. However, in view of the inaccuracy of colorimetric measurement in the early stages of the decomposition, the question as to whether *absolutely* no humin is formed directly from fructose, remains undecided.



It remained to take into account the constant occurrence of hydroxymethylfurfural among the decomposition products of fructose, as observed by Kiermayer.[1] That, however, this substance, again, is not directly produced from fructose, appears from the following consideration: Hydroxymethylfurfural is present at any time during the decomposition only in small quantities. Kiermayer showed that, in the presence of acids, pure hydroxymethylfurfural is rather rapidly decomposed into formic and levulinic acids, which indicates that the acids of fructose decomposition are likewise the immediate offspring of hydroxymethylfurfural. If, now, hydroxymethylfurfural itself came directly from fructose, its rate of formation would diminish with the disappearance of the sugar, and the result would be a correspondingly diminishing rate of formation of the acids. As a matter of fact, the rate of acid formation, as shown above, is not decreasing, but increasing. Hence hydroxymethylfurfural appears to come, not from fructose itself, but from some substance into which the sugar is first transformed and whose amount in solution increases during the earlier stages of the decomposition.

Remembering, finally, that no humin-like substance is known to be produced from hydroxymethylfurfural, and barring the formation of still other intermediate products as yet undetected, the mechanism of the decomposition of fructose by acids may therefore be pictured by the following scheme:

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[1] *Loc. cit.*

$$\begin{tikzcd}
 & \text{Hydroxymethylfurfural} \arrow[r] & \text{Formic and levulinic acids} \\
\text{Fructose} \arrow[r, shift left] & \text{Levulosin} \arrow[l, shift left] \arrow[u] \arrow[r] & \text{Humin}
\end{tikzcd}$$

Other substances than those mentioned in this scheme have, as just stated, not yet been isolated. That, however, the scheme does not fully represent the mechanism of fructose decomposition, and that at least one further intermediate compound—more or less ephemeral—must form, is clearly indicated by a further step to which the employment of the kinetic method has led. Early in the study I undertook to ascertain how many fructose molecules take part in the decomposition reaction. Two solutions were prepared. One (already mentioned above) contained, in a total volume of 300 cc., 231 g. of water and 100 g. of fructose. The second contained, in the same volume, again 231 g. of water and only 50 g. of fructose, the volume occupied in the first solution by the additional 50 g. of fructose, being in the second solution filled with 47.8 g. of mannitol. Both solutions were 0.7453-normal with respect to hydrochloric acid. This procedure for making the pair of solutions exactly equal in both acid and water concentration and differing in sugar concentration only, is similar to that recently employed by Rosanoff, Clark and Sibley[1] in a study of the order of the sugar hydrolysis reaction. The progress of the reaction in the first of the two solutions is already recorded in Table I, above, and graphically represented by Curve A, of Fig. 1. The progress of the reaction in the second solution is shown by Curve B of the same Fig. 1 and is numerically recorded in Table III:

TABLE III.—300 CC. OF THE SOLUTION CONTAINED 50 G. FRUCTOSE, 231 G. WATER AND 47.8 G. MANNITOL, AND WAS 0.7453-NORMAL WITH RESPECT TO HYDROCHLORIC ACID.

Time in hours	Rotation	Per cent change	Time in hours.	Rotation	Per cent. change.
0	—42.25°	0	3.0	—40.2°	4.8
0.5	—41.8	1.0	4.0	—39.7	6.0
1.0	—41.45	1.9	6.0	—39.0	7.7
1.5	—41.1	2.7	7.0	—38.75	8.3
2.0	—40.8	3.4	8.0	—38.5	8.8

In general, if *n* molecules of a substance take part in a reaction, and the initial concentrations of that substance in two given cases are respectively, *a* and *b*, then the rates of disappearance of the substance in the two cases are respectively described by the following equations:

$$\frac{dx}{dt} = k\,(a-x)^n \quad \text{and} \quad \frac{dx}{dt} = k\,(b-x)^n,$$

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[1] THIS JOURNAL, 33, 1911 (1911)

where x is the amount that has disappeared at the time t, and k is the velocity coefficient of the reaction at the given temperature. If the rate of disappearance is expressed in *percentages* of the initial quantities, as is generally done, then the two equations must be written in the form:

$$\frac{d \log (a - x)}{dt} = k\,(a - x)^{n-1} \text{ and } \frac{d \log (b - x)}{dt} = k\,(b - x)^{n-1}.$$

Denoting these two relative rates of change by the symbols V_a and V_b we get from the two equations, by sample algebraic transformation:

$$n = 1 + \left[\log \frac{V_a}{V_b} : \log \frac{a - x}{b - x}\right]$$

If the decomposition of fructose were not complicated by the consecutive reactions discussed above, this equation might be employed with reference to any moment in course of the decomposition. But in view of the complicating reactions that set in as soon as levulosin has made its appearance, the equation might be legitimately applied only with reference to the first instant of the fructose change, when nothing but pure fructose is present and that is just entering the first stage of the decomposition reaction. At that instant $x = 0$ and the equation just given becomes·

$$n = 1 + \left[\log \frac{V_a}{V_b} : \log \frac{a}{b}\right]$$

In the solutions under consideration the initial concentrations, a and b, of fructose were respectively, 100 and 50 g. per 300 cc.; their ratio, therefore, was exactly 2. The ratio $V_a : V_b$ at the point $t = 0$ was obtained with the aid of curves A and B of Fig. 1 by reading off the two x's (observed percents change) corresponding to the time $t = 2$ hours and dividing the greater x by the smaller, then reading off the x's for the time $t = 4$ hours, etc. These *x ratios* were next plotted against the corresponding times, and the resulting curve (nearly a straight line) was extrapolated to the axis $t = 0$, the point of intersection of this axis giving the required ratio $V_a : V_b$ at the time $t = 0$. This ratio was found to be about 2.03. Hence, by the equation just given, $n = 2.02$. In other words, *the first step in the change of fructose by acids is a bimolecular reaction.* Since, as is shown above, the molecular weight of levulosin corresponds to only $C_6H_{10}O_5$, the conclusion may be drawn with considerable certainty that the change of fructose into levulosin proceeds through the intermediate formation of a *disaccharide*, which changes reversibly into fructose as well as into levulosin. That this disaccharide should escape detection is not strange if one bears in mind that disaccharides usually undergo very nearly complete decomposition in the presence of acids.

In the kinetic study just outlined, two solutions were employed in which the concentrations of both acid and water were the same. Considered as reaction media, the two solutions were similar, on account of the physico-chemical similarity of fructose and mannitol. The solutions were so made up for the purpose of avoiding any such catalytic effect of water as has been observed in the case of sugar hydrolysis, and in this manner I was able to determine exactly the order of the decomposition reaction with respect to fructose. In order, however, to find out whether water would really have any specific effect, a still further experiment was instituted, employing a solution containing the same relative amounts of acid and of fructose as the one into which mannitol had been introduced, but this time replacing the mannitol by water. The results are numerically recorded in Table IV and are graphically represented by Curve C of Fig. 1.

TABLE IV.—600 CC. OF SOLUTION CONTAINED 100 g. FRUCTOSE AND 526 g. WATER AND WAS 0.7453-NORMAL WITH RESPECT TO HYDROCHLORIC ACID.

Time in hours.	Rotation.	Per cent. change.	Time in hours.	Rotation.	Per cent. change
0.0	-41.5°	0.0	7.75	-38.0°	8.4
0.5	-41.15	0.8	8.75	-37.7	9.1
1.0	-40.8	1.7	9.75	-37.45	9.8
1.5	-40.5	2.4	10.75	-37.25	10.2
2.0	-40.2	3.1	11.75	-37.05	10.7
2.5	-40.0	3.6	12.75	-36.85	11.2
3.0	-39.7	4.3	14.75	-36.45	12.1
3.5	-39.5	4.8	17.75	-35.95	13.3
4.0	-39.2	5.5	21.00	-35.45	14.6
4.5	-39.0	6.0	26.00	-34.75	16.2
5.5	-38.7	6.7	32.00	-34.55	16.7
6.75	-38.3	7.7			

Curves B and C in Fig. 1 show that water has a distinctly depressing effect on the velocity of decomposition. This might be expected in view of the reversibility of the fructose-levulosin transformation, the fructose molecule being levulosin *plus* the elements of water. That, however, besides this expected mass action, water exerts also a special catalytic effect, is plain from the fact that Curves B and C start out at appreciably different angles from the very point $t = 0$. Since in the beginning no levulosin is present, the water can exert no mass action, and therefore its depressing effect upon the initial velocity of the reaction can only be considered as negatively catalytic. We have, then, here another reaction in which water acts as a negative catalyzer, as it does in the case of sugar hydrolysis.[1]

3. Decomposition of Fructose by Acids at Ordinary Temperatures.

The physico-chemical conditions employed were now changed to resemble more closely those likely to be maintained in sugar hydrolysis experiments. A new set of solutions was exposed to the temperature of the laboratory. The kinetic experiments described above had shown the decomposition of fructose to be a bimolecular reaction and hence to proceed at a relative speed proportional to the sugar cencentration. In view of this result, it was necessary to investigate a series of solutions varying in fructose content up to the highest limit that may be expected to occur in sugar hydrolysis work, namely, about 30% of fructose, corresponding to about 60% of uninverted cane sugar. Two acids were employed, for reasons already stated in the introductory section above. The strength of formic acid was varied up to four times normal, that of hydrochloric up to about one-half normal.

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[1] Rosanoff and Potter, THIS JOURNAL, 35, 248 (1913).

In the case of hydrochloric acid it will suffice to mention only the most significant results: (*a*) A solution containing about 19% of fructose and about 0.089 mols HCl per liter showed an initial rotation of —49.8°. Four days later the rotation was exactly the same. When the solution had stood for fifteen days, the observed rotation was —49.7°. Thus, when cane sugar is inverted with 0.1-normal hydrochloric acid at ordinary temperatures, the final rotation is attained long before an appreciable decomposition of the fructose present has set in, even if the original cane sugar solution be not less than 40% strong. No correction of the observed final rotation is required. (*b*) A solution containing about 20% of fructose (*i. e.*, corresponding to a 40% cane sugar solution), and 0.447 mols HCl per liter showed an initial rotation of —51 9°. It was found to change at the rate of about 0 09° Ventzke per 24 hours. With such a solution, a day is more than sufficient for obtaining the required final reading, and as a change of 0.09° V. in that final rotation has no appreciable influence upon the magnitude of the hydrolysis constant, it is plain that at least the fructose decomposition calls for no correction. In still stronger hydrochloric acid solutions a rapid appearance of color and decrease of rotation was observed. But solutions stronger than half-normal with respect to hydrochloric acid, and containing more than 40% of cane sugar, are not likely to be employed in studies of the velocity of hydrolysis.

In the case of formic acid it was found: (*a*) Strong fructose solutions 0.4-normal with respect to formic acid suffer no change in rotation in 77 days, probably in a much longer time yet; (*b*) Strong fructose solutions 0.8-normal with respect to formic acid likewise undergo no detectable change in 77 days. (*c*) *Double-normal* formic acid produced in 77 days no change in solutions containing respectively, 14%, 16% and 25% of fructose. Even in a 28% solution, corresponding to about 56% of cane sugar, the change produced by double-normal formic acid in 77 days was scarcely sufficient to affect the calculated velocity coefficient of sugar inversion. Moreover, as experience in the Clark University laboratories has shown, forty days are far more than sufficient for the attainment of the "infinity" reading in formic acids of usable strength.

4. The Decomposition of Glucose by Acids at 75°.

The experimental method exployed in the case of glucose was for the most part similar to that described above in connection with fructose. In the case of glucose it was found to be more convenient to use monochromatic light in measuring the changes of rotation. As a source of extremely brilliant sodium light a polarimeter lamp was used devised by M. A. Rosanoff and kindly placed by him at my disposal. The temperature of the thermostat, on account of the slower decomposition of glucose, was set at 75°, as compared with the 60° employed in the case of fructose. No boneblack was employed.

At lower temperatures and under the influence of concentrated hydrochloric acid, glucose condenses to the disaccharide isomaltose, as shown by Emil Fisher.[1]

The question now arose whether the same condensation would take place under the very different conditions of my own experiments. A solution containing per liter 500 g. of glucose and 0.7 mols HCl was kept for 48 hours at 75°. The insoluble humin formed was filtered off, and the dark brown filtrate was rendered neutral with an excess of silver hydroxide. The organic silver salts now in the solution were decomposed with hydrogen sulfide and the solution freed from the latter by boiling. After diluting and nearly neutralizing with sodium hydroxide, brewer's yeast was added and the solution allowed to stand at 32–35°. The rotation of the solution, originally 40°, was found at the end of 60 hours to have fallen to 18.9°. Subsequently no further change could be detected. A solution containing nothing but pure glucose, when similarly treated with yeast, lost its rotation completely. Obviously, the solution under investigation had contained another active substance beside glucose. To isolate that substance, the solution was separated from the yeast by filtration, evaporated *in vacuo*, to a thick sirup, and precipitated with 95% alcohol. The precipitate was redissolved in a small amount of water and about three-quarters of it again precipitated out with alcohol. The new precipitate was treated in the same way. The precipitate obtained in this last operation was again dissolved in water, alcohol was added to incipient precipitation, the first amount of precipitate formed was removed, then the precipitation was completed by the addition of an equal volume of ether. Finally, the precipitated sticky substance was transferred to a smaller vessel by once more dissolving in a small amount of water and then evaporating and drying the residue *in vacuo* over phosphorus pentoxide. The residue was identified as isomaltose, which is now generally accepted to be identical with the "gallisin" of Schmitt and Rosenhek.[2] Two cryoscopic determinations gave the molecular weights, respectively,

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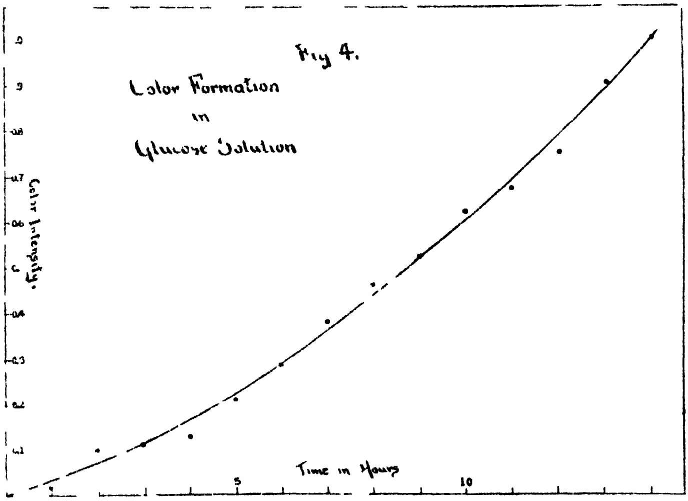
[1] *Ber.*, 23, 3687 (1890).

[2] *Ibid.*, 17, 2456 (1884).

326 and 332, in sufficient agreement with the theoretical molecular weight of isomaltose, 342. The specific rotation of the substance in 4.62% solution was found to be $[\alpha]_D = 84.1°$. According to a formula given Schmitt and Rosenhek, the rotation of a solution of that strength should be $[\alpha]_D = 84.4°$.

The question as to whether the humins are formed directly from glucose or from isomaltose was studied colorimetrically very much as in the case of fructose. The results are graphically represented by Fig. 4.



Since only glucose was present at first, the upward concavity of the curve demonstrates that humin is formed, not from glucose directly, but from some intermediate transformation product, possibly isomaltose itself, but perhaps more probably from an undetected transformation product of isomaltose, corresponding to the levulosin yielded by fructose. In this case again, if no humin whatever were formed from glucose directly, the curve would be tangent to the time axis at the origin. Such tangency is not indicated by the figure. The point, however, as in the case of fructose, must be considered as undecided in view of the comparative inaccuracy of the colorimetric observations in the early stages of the decomposition.

The formation of considerable amounts of isomaltose from glucose indicates that, unlike most disaccharides, which are hydrolyzed by aqueous acids all but completely, isomaltose undergoes hydrolysis to a distinctly limited extent, like esters. Under these circumstances it appeared possible to show that it is the isomaltose and not the glucose that changes into the later decomposition products, by studying the behavior of the two substances in separate solutions. Two solutions were prepared containing about 0.7 mol. of hydrochloric acid per liter and equivalent weights, respectively, of isomaltose and glucose. The two were placed in a thermostat kept at 100° and their changing rotations were observed at short intervals of time. The results are reproduced in Tables V and VI, and are graphically shown by Fig. 5. Time was reckoned in minutes.

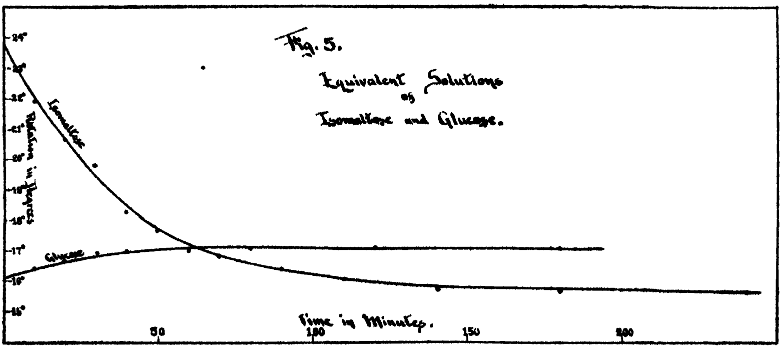
TABLE V.—100.36 g. SOLUTION CONTAINED 9.5919 g. ISOMALTOSE (2 × 0.0561 MOL) AND WAS 0.7453-NORMAL WITH RESPECT TO HYDROCHLORIC ACID.

Time in minutes.	Rotation.	Time in minutes.	Rotation.
0	23.75°	90	16.4°
10	21.95	110	16.1
20	20.65	140	15.7
30	19.8	180	15.7
40	18.3	240	15.65
50	17.7	300	15.65
70	16.9		

TABLE VI.—100.36 g. SOLUTION CONTAINED 10.0965 g GLUCOSE (0.0561 MOL) AND WAS 0.7453-NORMAL WITH RESPECT TO HYDROCHLORIC ACID.

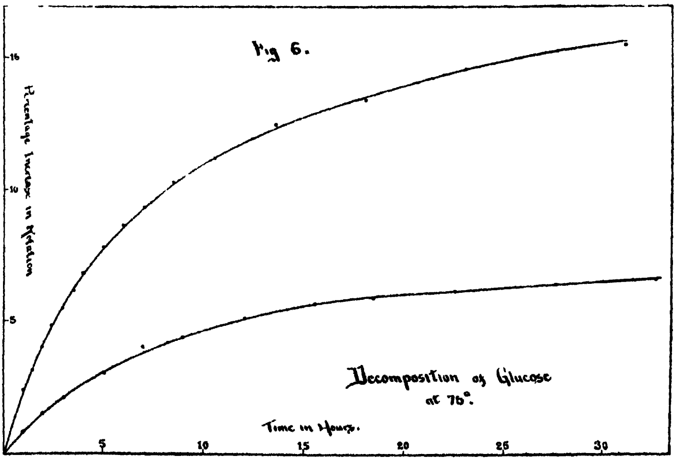
Time in minutes.	Rotation.	Time in minutes.	Rotation.
0	16.1°	60	17.0°
10	16.4	80	17.05
20	16.7	120	17.05
30	16.9	180	17.0
40	16.95		

If either of the substances merely changed into the other and underwent no further decomposition, the same rotation would finally be attained in both solutions, corresponding to the equilibrium point of the reversible reaction involved. In the figure, the two curves would run into coincidence with one and the same horizontal line. If it were the glucose that suffered decomposition, its curve would never rise high enough to attain that horizontal line, for the decomposition is attended with destruction of rotatory power. In that case, also, the curve corresponding to the isomaltose solution would be depressed. But while the depression for the glucose solution would, from the very beginning, be considerable, owing to the large amount of glucose present, and the consequently rapid rate



of its destruction, the depression of the curve of the isomaltose solution would in the early stages be very slight indeed, corresponding to the insignificant amount of glucose present and the consequently slight rate of its destruction. In other words, the upper curve in the figure would follow a practically unchanged course, while during the same time the lower curve would be considerably depressed. Instead, therefore, of soon merging into the horizontal equilibrium line, the two curves would be separated. But the figure indicates an entirely different phenomenon; the two curves *intersect* at an early stage of the process. This indicates that the actual change has depressed the upper curve far more than the lower one, *i. e.*, that the destruction of the rotatory power proceeded much faster in the isomaltose than in the glucose solution. The conclusion follows that it is the isomaltose that undergoes further decomposition and that any direct decomposition of glucose is very slight indeed, if it takes place at all.

In conclusion, the order of the glucose decomposition was investigated kinetically, to ascertain whether in this case also, as in that of fructose, the reaction is bimolecular in its early stages, indicating that the first step in the change is the formation of a disaccharide. Two solutions were prepared, containing, respectively, 150 and 75 g. of glucose per 300 cc. and both 0.7453-normal with respect to hydrochloric acid. The temperature was again 75°. Properly speaking, the two solutions should have also been made equal in water concentration, but this was not feasible on account of the limited solubility of mannitol, which I desired to employ as an equalizer of the volumes (as in the case of fructose above). The results are reproduced by Tables VII and VIII and by Fig. 6.



Owing to the larger amount of water in the more dilute solution, the lower curve is appreciably depressed (negatively catalytic effect of water), and the initial order of the reaction appears to be, not 2, but about 2.4. However, in view of the results in the case of fructose, there can be no serious doubt but that the glucose decomposition is strictly bimolecular in its earliest stages. Both monosaccharides, then, begin by changing into disaccharides, and next, probably, both disaccharides, by further loss of water, split up into molecules with six carbon atoms. In the case of fructose it is the disaccharide that decomposes with great rapidity, while its decomposition product levulosin, $C_6H_{10}O_5$, is comparatively stable. In the case of glucose, on the contrary, it is the disaccharide isomaltose, $C_{12}H_{22}O_{11}$, that is comparatively stable.

TABLE VII.—300 CC. OF SOLUTION CONTAINED 150 g. GLUCOSE AND 195 g. WATER AND WAS 0.7453-NORMAL WITH RESPECT TO HYDROCHLORIC ACID.

Time in hours.	Rotation.	Per cent change.	Time in hours.	Rotation.	Per cent. change.
0	79.15°	0	6.0	86.05°	8.7
1.0	81.1	2.5	7.0	86.60	9.4
1.5	81.7	3.2	8.5	87.35	10.4
2.0	82.35	4.1	10.5	88.10	11.3
2.5	83.0	4.9	13.5	89.05	12.5
3.0	83.55	5.6	18.0	89.8	13.5
3.5	84.1	6.3	23.0	90.8	14.7
4.0	84.6	6.9	31.0	91.5	15.6
5.0	85.4	7.9			

TABLE VIII.—ABOUT 300 CC. OF SOLUTION CONTAINED 75 g. GLUCOSE AND 244 g. WATER AND WAS 0.7453-NORNAL WITH RESPECT TO HYDROCHLORIC ACID.

Time in hours.	Rotation.	Per cent. change.	Time in hours.	Rotation.	Per cent. change.
0	39.0°	0	12.0	41.05°	5.3
1.0	39.35	0.9	15.5	41.25	5.8
2.0	39.6	1.5	18.5	41.35	6.0
3.0	39.85	2.2	22.5	41.45	6.3
5.0	40.20	3.1	27.5	41.6	6.6
7.0	40.60	4.1	32.5	41.65	6.8
9.0	40.75	4.5			

It may be added that in the stronger of the two glucose solutions just mentioned, the limit toward which the ratio *isomaltose: glucose* tends is about 2/3. In the more dilute solution that ratio appears to be roughly 1/5.

The final decomposition products of glucose, formic and levulinic acids, and a mixture of soluble and insoluble humins,[1] appear to be identical with those of fructose. On the other hand, as already stated above, the two acids are immediate decomposition products of hydroxymethylfurfural. The processes of decomposition in the case of glucose and of fructose would thus seem to be strictly analogous. The assumption that glucose is partly changed into fructose, recently made by H. Koenigsfeld,[1] is apparently without foundation.

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[1] Conrad and Guthzeit, *Loc. cit.* Kiermayer, *Loc. cit.* Van Ekenstein and Blanksma, *Ber.*, 43, 2355 (1910).

5. Decomposition of Glucose by Acids at Ordinary Temperatures.

The results of the preceding section show that glucose decomposes far less rapidly than fructose, and since it was found that even the rate of fructose decomposition is not rapid enough to vitiate the final polarimetric reading in ordinary sugar hydrolysis, it was to be expected that danger from the decomposition of glucose was to be feared even less. Nevertheless, a few experiments were instituted to test the point directly.

A solution containing 0.179 mol HCl per liter and no less than 52% of glucose showed no change in rotation in 12 days; in 25 days the rotation was found to have changed only slightly over 0.3%. Even a solution nearly 0.9-normal with respect to hydrochloric acid and containing 27% of glucose was found to have changed its rotation only 0.25% in 25 days. A solution similarly strong in hydrochloric acid and containing no less than 43% of glucose showed no change of rotation in 7 days, and only 0.2% change in 12 days. Similarly, a solution containing 28% of glucose and two mols of formic acid per liter showed a change in rotation of only little over 0.2% in 76 days. Finally, a 24% solution of invert sugar containing two mols of formic acid per liter did not show the slightest change of rotation in 76 days. It is thus plain that under all ordinary circumstances the observed "final" rotation of an inverting sugar solution is entirely reliable and needs no correction.

In conclusion, I wish to thank Professor M. A. Rosanoff, of Clark University, for invaluable help in preparing this paper. It is further a pleasure to express my appreciation to Dr. W. G. Lyle and Mr. P. A. Kober of this laboratory for their kindly interest in the work.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO.]

THE ACTION OF ACETIC ANHYDRIDE ON SOME BENZYLIDENE ANTHRANILIC ACIDS. III.

BY JOHN B. EKELEY AND L. CECIL SLATER.

Received January 10, 1914.

Ekeley and Dean[2] and Ekeley and Clinton[3] have shown that acetic anhydride reacts with benzylidene anthranilic acids with the formation of acetylketodihydrobenzmetoxazines, according to the following reactions:

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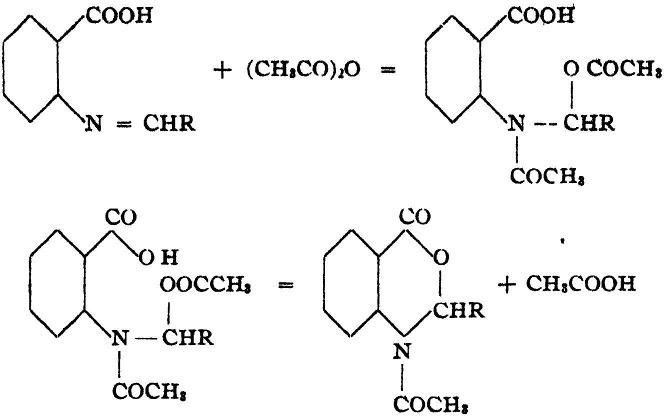
[1] *Biochem. Z.*, 38, 310 (1912)

[2] THIS JOURNAL, 34, 161.

[3] *Ibid.*, 35, 282.



This paper will describe the benzylidene anthranilic acids obtained from *o*-chlorobenzaldehyde, *m*-chlorobenzaldehyde, *p*-chlorobenzaldehyde, *m*-toluylaldehyde, *p*-toluylaldehyde, and *m*-oxybenzaldehyde, and the benzmetoxazines obtained from them by means of acetic anhydride.

o-Chlorobenzylideneanthranilic Acid.—This benzylidene product separates out in solid form, when molecular proportions of anthranilic acid and *o*-chlorobenzaldehyde are brought together in cold alcohol solution. Recrystallized from alcohol, it yields colorless crystals. M. p. 130°.

Calc for $C_{14}H_{10}O_2NCl$. N, 5 39, found N, 5 0.

o-Chlorophenylacetketodihydrobenzmetoxazine.— *o*-Chlorobenzylideneanthranilic acid was heated with a slight excess of acetic anhydride on the water bath for several hours. On cooling the solution, the oxazine crystallized out in colorless crystals, which, after being pressed out on a porous plate, were recrystallized from benzene. M. p. 154°.

Calc. for $C_{16}H_{12}O_3NCl$ N, 4 64, found N, 4 62

m-Chlorobenzylideneanthranilic Acid.—The aldehyde and acid react in cold alcohol solution, so that in a few minutes the solid acid may be filtered off, pressed out on a porous plate, and recrystallized from toluene. Colorless crystals. M. p. 174°.

Calc for $C_{14}H_{10}O_2NCl$: N, 5.39; found N, 5 39.

m-Chlorophenylacetketodihydrobenzmetoxazine.—The above benzylidene anthranilic acid was heated several hours on the water bath with an excess of acetic anhydride. The excess anhydride was driven off by heating the reaction mixture with methyl alcohol, after which, on cooling the product, the oxazine crystallized out. Recrystallized from methyl alcohol, it yielded colorless crystals. M. p. 171°.

Calc. for $C_{16}H_{12}O_3NCl$: N, 4 64; found. N, 4 4.

p-Chlorobenzylideneanthranilic Acid.—Molecular proportions of *p*-chlorobenzaldehyde and anthranilic acid were allowed to react by pouring the molten aldehyde into a concentrated alcohol solution of the acid. Recrystallized from alcohol, the reaction product gave colorless crystals. M. p. 136°.

Calc. for $C_{14}H_{10}O_2NCl$: N, 5.39; found: N, 5 4

p-Chlorophenylacetketodihydrobenzmetoxazine.—This was obtained in the same manner as the corresponding *o-* and *m*-compounds. The crude product was recrystallized from benzene. Colorless crystals. M. p. 187°.

Calc. for $C_{16}H_{12}O_3NCl$. N, 4.64; found. N, 4.8

m-Toluylideneanthranilic Acid.—*m*-Toluylaldehyde reacts with anthranilic acid in concentrated alcohol solution in the cold. On allowing a small quantity of the solution to evaporate on a watch glass, crystals are obtained which, on being added to the original solution, caused it to solidify. The crude acid after being pressed out on a porous plate and recrystallized from alcohol yielded colorless crystals. M. p. 149°.

Calc. for $C_{15}H_{13}O_2N$: N, 5 57; found: N, 5 5

m-Methylphenylacetketodihydrobenzmetoxazine.— *m*-Toluyleneanthranilic acid was heated with an excess of acetic anhydride at a temperature just below the boiling point of the anhydride for four hours. At the end of that time the vapor of the anhydride was drawn off by suction until the solution was concentrated enough to yield crystals, when a small amount was removed and treated with a drop of methyl alcohol on a watch glass. On seeding the original solution with these, the oxazine crystallized out. It was recrystallized from benzene, yielding colorless crystals. M. p. 145°.

Calc. for $C_{17}H_{15}O_3N$. N, 4 98; found. N, 4 62

p-Toluylideneanthranilic Acid.—*p*-Toluylaldehyde reacts with anthranilic acid in cold alcohol solution. A small amount of the solution was placed on a watch glass and allowed to evaporate. The original solution was seeded with the crystals thus obtained, whereupon the *p*-toluylideneanthranilic acid crystallized out. Yellowish crystals from alcohol. M. p. 131°.

Calc. for $C_{15}H_{13}O_2N$: N, 5 57; found. N, 5 5

p-Methylphenylacetketodihydrobenzmetoxazine.—This compound was prepared in a manner analogous to that used in the case of the corresponding *m*-compound. The crude product, recrystallized from methyl alcohol, gave colorless crystals. M. p. 121°.

Calc. for $C_{17}H_{15}O_3N$· N, 4 98; found: N, 4 76

m-Oxybenzylideneanthranilic Acid.—This compound was prepared from *m*-oxybenzaldehyde and anthranilic acid in a manner analogous to the methods used in the preceding cases. Yellow crystals from alcohol. M. p 175°, with decomposition.

Calc. for $C_{14}H_{11}O_3N$: N, 5 80; found: N, 5.6.

Acetyl-m-oxyphenylacetketodihydrobenzmetoxazine.—This was prepared as in the other cases by treating the above benzylideneanthranilic acid on the water bath with an excess of acetic anhydride. In this case, as in the case of the corresponding *o*- and *p*- compounds described by Ekeley and Dean,[1] the hydrogen of the phenol group has been replaced by acetyl. The crude compound was recrystallized from benzene, yielding colorless crystals. M. p. 124°.

Calc for $C_{18}H_{15}O_5N$: N, 4.31; found: N, 3.99.

Repeated attempts to obtain oxazines using anisylaldehyde, piperonal, and furfuryl aldehyde have failed. It is not clear wherein the difficulty lies.

BOULDER, COLORADO

NOTE.

A Case of Potassium Cyanide Poisoning.—Certain data recently obtained in a toxicological investigation seem worth putting on record. A man died from drinking whisky containing an unknown amount of potassium cyanide. The autopsy was performed about six hours after death, and the stomach and intestine placed in glass jars, where they remained unopened until four days after death, when the analysis was commenced.

Potassium cyanide was determined by the well-known method of acidifying with tartaric acid and distilling with steam, adding borax to the distillate and distilling again, and then treating this distillate with silver nitrate to precipitate silver cyanide, which was filtered out, dried, and weighed.

The stomach measured nine and one-half inches along the lesser curvature, and twenty-five and one-half inches along the greater. There were dark areas along the greater curvature, and the wall in places was abnormally red. The rugae were well obliterated. The contents were acid to litmus, and consisted of an undigested meal. The weight of the stomach wall was 288 grams, and of the stomach contents 1014 grams.

A portion of the stomach contents weighing 349 grams, in which hydrocyanic acid was determined five days after death, showed that for the whole stomach contents 0.053 gram potassium cyanide would have been necessary to produce the amount of hydrocyanic acid present. A portion of the intestine analyzed at the same time gave no cyanide. To test the rate of decay of the hydrocyanic acid in the stomach contents, the unused material was placed in a glass stoppered bottle and allowed to stand for several weeks. A portion weighing 143 grams, analyzed 23 days after death, gave 0.039 gram potassium cyanide for the whole stomach contents. A third portion, weighing 310 grams, analyzed 76 days after death, showed no hydrocyanic acid present. The material showed no marked decomposition.

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[1] THIS JOURNAL, 34, 164.

A portion of the stomach wall, about one square inch in area, taken when the analysis was begun four days after death, extracted with 0.4% hydrochloric acid gave a solution which did not dissolve fibrin. A solution from a stomach wall where death has been due to natural causes will ordinarily do so after that length of time. M. P. CRAM.

BOWDOIN COLLEGE, BRUNSWICK, MAINE

CORRECTION.

THE MOLECULAR REARRANGEMENT OF TRIARYLMETHYLHYDROXYLAMINES AND THE "BECKMANN" REARRANGEMENT OF KETOXIMES.

BY JULIUS STIEGLITZ AND PAUL NICHOLAS LEECH.

Through an oversight in the final editing we have given (Vol. XXXVI, p. 297) the proportions by weight of aniline hydrochloride and chloroaniline hydrochloride obtained in the rearrangement of parachlorophenyldiphenylmethylhydroxylamine. The molal ratios are:

Line 24, 28% chloroaniline, 72% aniline.
Line 29, 31.5% chloroaniline, 68.5% aniline.
Line 30, 28% chloroaniline, 72% aniline.

The provisional conclusion based on these results (p. 287), that "roughly two-thirds" of the substance rearranges to form aniline and one-third to form chloroaniline is little affected by this correction.

CHICAGO, Feb. 7, 1914

NEW BOOKS.

A Textbook of Chemistry. By WILLIAM A. NOYES, Director of the Chemical Laboratory of the University of Illinois. Henry Holt & Co., New York, 1913. xv + 602 pp. 13.5 × 20.5 cm. Price, $2.25.

This new text by Professor Noyes marks a decided step forward in the presentation of the facts and theories of general chemistry. The brief introduction and very early entrance upon equations (p. 21) are special features of the book. The usual discussions on the gas laws follow in close order with good illustrations, but, in the minds of the great majority of chemists, it is doubtful if Avogadro's hypothesis (here called a law) would be construed as other than an hypothesis. It is pleasing to note the absence of the term "equivalent weight," a term that has too long outlived its usefulness and only served for the confusion of the beginner. Graphical formulas meet with an early introduction, simplifying remarkably such discussions as the Weldon process for chlorine. The chapter on the Periodic System is introduced just after chlorine and preceding the chapter on the halogen family (Chapter X). It is surprising that the oxygen acids of bromine receive so little mention and the oxides and oxygen acids of iodine none at all. The formulas, ClO_2 and NO_2, represent dioxides and not peroxides, if our acccepted definition, likewise acceded to by the author, is correct. The Phase Rule, first discussed in the study of water, is made to serve the student in the study of chlorine hydrate, plaster of Paris, and in other instances. Furthermore an interesting exposition of the electron theory is made to explain the formation of sulfurous and sulfuric acids from their anhydrides, the phenomena of ionization, the formation of ammonium salts and the functionary properties of the metals. It is well, however, for the elementary student that the paragraphs on the Phase Rule, at least, are marked with an asterisk and left to the discretion of the instructor. At the end of Chapter XI on sulfur a number of the figures representing crystal systems are inverted and others show poor alignment; the term "regular" system is a misnomer for cubic system—all systems are regular. Chapters XII to XV include a systematic study of the elements of group V of the Periodic System, whereas chapters XVI to XX are given over to the study of carbon and its derivatives, with chapter XXI concluding the study of the elements of group IV. The careful attention given to the ionization of hydrogen sulfide (pp. 167–70), and of orthophosphoric acid (pp. 250–2), as well as to colloidal solutions (pp. 262–3) and to a method for the determination of the atomic weight of an element (p. 130), deserve especial praise. Professor Noyes suggests the term "Formular" (p. 183) for solutions containing per liter one formular weight. This seems indeed more desirable than the oft-used "molar" in that the exact formula, simple or polymeric, upon which the solution is based, must also be given. In no text on general chemistry does the subject of carbon receive such full and ample treatment as is contained in these few chapters. The alcohols, aldehydes, ketones, acids, carbohydrates, amines, dyes, alkaloids, and proteins receive a brief but systematic and clear presentation, and contribute greatly to the store of knowledge which should be readily accessible to a student undertaking the study of a truly "general" chemistry. Chapter XXII introduces a study of the metals in relation to the non-metals; here also is to be found an excellent discussion on the role of indicators. The subject of amphoteric electrolytes might better have been given a short discussion, with illustrations, at this point in order to avoid repeated definitions at every recurrence throughout the text (pp. 206, 265, 483, 499). In the chapters on the metals (XXIII to the final XXXIII inclusive) many recent discoveries have been described. Thus, together with brief descriptions of all the rare metals and their uses we find also stated: A new method for preparing aluminium oxide from clay, the fireproofing of cotton goods, Werner's theory for the two isomeric hydrates of chromic chloride and also for the cobalt amines, the improvements in the open hearth process for steel, the detection of nickel as nickel dimethylglyoxime, etc. Throughout the text, numerous questions are submitted to the student. These, we fear, too often must find answers in larger reference volumes. Thus the difference in action of sulfuric acid toward potassium bromide and potassium chloride is noted, but the final and more complicated reaction toward potassium iodide is made a problem for the student (p. 145). The author, moreover, is inclined to open discussions upon certain classes of compounds before any actual description of the several members. For example, the hydrides of Group V are studied in connection with phosphine; again the properties of antimony and bismuth sulfides are discussed with arsenic sulfide, etc. These and many of the theoretical considerations stamp the text as one primarily for the advanced student—such discussions necessarily broadening his knowledge and extending his vision over the field as a whole; but for the student without previous training his all too short powers of vision are more than likely to be strained and he himself lost in an interminable forest. For such, however, the volume will admirably serve as a reference text. It is to be regretted that the many citations to the literature are placed in the body of the text instead of in the less conspicuous footnote. The exercises at the end of the chapters are excellent, comprising a wealth of material alike instructive to all. In the exercises on pages 156–9 the method of constructing graphical formulas is given with a clearness and detail found in but few texts. Indeed, this volume by Professor Noyes stands unique among texts on general chemistry in the wide application made of graphical formulas; a question open often to objections if too far pressed but one that can hardly fail to appeal to the students' imagination and to impress where other means have failed. The text is comparatively free from misprints, well indexed, clearly printed and serviceably bound.

W. J. HALE.

Mesure de la vitesse de la lumière. Etude optique des surfaces. Mémoires de LEON FOUCAULT. Paris: Armand colin. pp. 122, 12 × 20 cm. Paper. Price, 1.30 francs.

This publication is volume II of the series of scientific classics published under the direction of H. Abraham, H. Gautier, H. Le Chatelier and J. Lemoine. The pamphlet presents a brief biographical sketch of Foucault and his original researches on the velocity of light and on optical surfaces. It is gratifying that these classical papers are thus made available to a larger circle of scientists. Their content is, of course, primarily of interest to the physicist.

L. KAHLENBERG.

Mendelejeff's Periodic System of the Elements. By JOHN NESBIT SWAN, Monmouth College, Monmouth, Illinois. Price for sample copy $0.10, 100 copies for $5.00.

The symbols and atomic weights of the elements arranged in the periodic system are printed on a card 35 cm. square, with the thought that students might have these cards in their rooms and that frequent reference to such a card would be useful. W. A. N.

Eau oxygénée et ozone. Mémoires de THENARD, SCHOENBEIN, DE MARIGNAC, SORET, TROOST, HAUTEFEUILLE, CHAPPUIS Paris: Armand Colin. pp. 111, 12 X 20 cm. Paper. Price, 1.20 francs.

This is volume III of the series of scientific classics just mentioned. The editors have rendered a real service in thus bringing together and presenting in an attractive form the masterly work of Thenard on hydrogen peroxide, and the papers of Schoenbein, Marignac, Soret, Troost, Hautefeuille and Chappuis on ozone. These papers have appeared in the *Comptes Rendus* and the *Annales de Chimie et de Physique*. Besides presenting the original researches, the publication contains a brief biographical note of each author. The very interesting letters of Schoenbein to Arago, and of Marignac to Dumas are also presented. These classical researches which have thus become available to many readers in an attractive form, should certainly prove to be a source of inspiration to students of chemistry. The editors are to be congratulated upon their work. L. KAHLENBERG.

From the Letter-Files of S. W. Johnson. Edited by his daughter, ELIZABETH A. OSBORNE. Yale University Press, 1913. pp. 292. $2.50 net.

Rare indeed in the biographical contributions of the present day are the instances where the letters and papers of a distinguished man of science are either available or suitable to give a comprehensive picture of his personality. Biographies are, as a rule, individual estimates fortified here and there by the more objective impressions which surviving fragments of what the subject has said or done may afford. With commendable judgment and critique Mrs. Osborne has succeeded in making the selections from the letter-files of her honored father tell the story of his aspirations and his struggles in the varied fields of effort that he entered. They bring into relief his trials and victories in the days when modern chemistry had its beginnings in America; they give an impression of the character and temperament of a man with a high purpose, and of the surroundings and circumstances in which he chose to live and work. Out of a wealth of material represented by long treasured human documents, interspersed with the discriminating explanatory narrative of a devoted admirer of scientific work, has been spun the account of how young Americans entered the world of scientific endeavor two generations ago. We get glimpses of Erdmann, Liebig, von Kobell and other worthies in their European homes. Then follows the story of some of the early struggles of the school of science at Yale. But the chief interest centers in the foremost activity with which the name of Professor Johnson is to be associated, namely, the propaganda and unflagging campaign resulting in the establishment of the system of Agricultural Experiment Stations in the United States. The Station started in Connecticut in 1877, and of which Professor Johnson was the first director, was the earliest permanent organization of the kind in America, the forerunner of the splendid movement which has prepared the way for the application of scientific methods and results to the improvement of Agriculture. No man has felt more keenly than Professor Johnson that the professional agriculturalist trained in science is "the indispensable instrument for the agricultural salvation of our country." Two of Professor Johnson's books: "How Crops Grow" and "How Crops Feed" have probably been more widely read than any other American work on Agricultural Chemistry. They were devoted to the belief that "agricultural chemistry has ceased to be the monopoly of speculative minds and is well based on a foundation of hard work in the study of facts and first principles."

A few references of this sort must here suffice to recall the debt which chemistry in America owes to the modest yet forceful writer and organizer, the chemist and science-preacher who died in 1909. This biographical volume is the engaging narrative of a useful career, certain to bring cheerful recollections to the older chemists and engender inspiring reflection among the younger workers of this country. LAFAYETTE B. MENDEL.

Jacobus Henricus van't Hoff; sein Leben und Wirken. VON ERNST COHEN, Professor an der Reichs-Universität zu Utrecht. Mit zwei Gravüren und 90 Abbildungen. pp. 638. Leipzig: Akademische Verlagsgesellschaft m. b H., 1912. Price, 16 Marks.

This life of van't Hoff by his long-time assistant and friend, Ernst Cohen, is literally a "labor of love." Cohen knew van't Hoff as few others have known him, and here plays somewhat the role of Boswell to his master.

The characteristics which marked the subsequent career of van't Hoff—independence of thought and action—early manifested themselves. The modern writers appealed to this Dutch youth more than the ancient; and he seems to have been greatly influenced by Byron, Burns and Heine.

In chemistry, van't Hoff's originality soon began to assert itself. He went to Bonn at the age of 20 to work with Kekulé, who was then at the height of his career; but the chemistry of Kekulé did not appeal to van't Hoff; it did not appear to him to lead anywhere. It dealt systematically with the beginning and end of chemical reactions, but disregarded the intermediate stages, which, to van't Hoff's mind, were the most important.

Van't Hoff, after a short stay with Kekulé, in Bonn, and Würtz in Paris, returned to Holland to work out his own chemistry. The result was that at the age of 22 he published a brochure of eleven pages in Dutch, which was the beginning of stereochemistry, or chemistry in three dimentional space, and which was destined to become the philosophy of the chemistry of carbon.

His next great work was in connection with the velocity and equilibria of chemical reactions; and this was followed in 1887 by what is now regarded as van't Hoff's greatest contribution to science; the applicability of the gas laws to the osmotic pressure of solutions.

It is worth noting that van't Hoff, being born in 1852, had published three epoch-making contributions to chemistry when only thirty-five years old.

The book in question deals not only with these, but with the lesser contributions of van't Hoff to chemical science. Cohen's life of van't Hoff is written in that clear and interesting style, for which its author is distinguished. The genuine enthusiasm and admiration of the student for his teacher, of the coworker for his master, not only one of the very greatest chemists, but one of the greatest men of science of all times, pervades the entire work and gives to it a peculiar life and charm.

HARRY C. JONES.

Theories of Solutions. SVANTE ARRHENIUS pp xx and 247. Yale University Press, $2 25 net. (Second printing)

This volume contains the Silliman lectures delivered by Arrhenius at Yale in 1911; its scope is best indicated by the chapter headings: Short History of the Theory of Solutions; The Modern Molecular Theory; Suspensions; The Phenomena of Adsorption; The Analogy between the Gaseous and the Dissolved State of Matter; Development of the Theory of Electrolytic Dissociation; Velocity of Reactions; Conductivity of Solutions of Strong Electrolytes; Equilibria in Solutions; The Abnormality of Strong Electrolytes; The Doctrine of Energy in Regard to Solutions. In these lectures the author tries "to exhibit such facts as have not in a higher degree attracted the attention of the authors of text-books in this branch, and thereby to give a broader and more complete view of the exceptionally fertile field which we cultivate." From this, and from the above list of headings, one would expect to find the whole subject treated with a breadth of view not usually found in discussions of this general topic; and this expectation the reader will find to be amply realized. In any critical survey of such a controversial field, there are sure to be individual differences of opinion on points the definite elucidation of which will require further, and appropriate, experimental work; but the reviewer knows of no better presentation of the subject matter, and of none in which the relations betwen so many different lines of evidence are marshalled and the substantial concordance of the conclusions derived from these various lines so well shown forth. The value of the book is enhanced by a bibliographical list, covering twelve pages and containing many references not commonly known, and by good indices of subjects and authors.

JOHN JOHNSTON.

Radioaktive Substanzen und ihre Strahlungen. By E. RUTHERFORD. Akademische Verlagsgesellschaft: Leipzig, 1914. p. 642.

This book constitutes Vol. 2, of the Handbuch der Radiologie edited by Dr. Erich Marx of the University of Leipzig. Vol. 1 on "Die Ionisation der Gase" will shortly be issued. Vol. 3, "Die Glimmentladung, die Kathoden und Röntgenstrahlung, und der lichtelektrische Effekt," and Vol. 4, "Theorie des Elektrons und der Röntgenstrahlung" will appear later. The present volume is a straight translation of Rutherfords "Radioactive Substances and their Radiations," without changes or additions of any kind. This book is now too well known to require further description. The translation was made by Prof. Marx under the supervision of Prof. Rutherford. R. B. MOORE.

Metallographie. Ein ausführliches Lehr- und Handbuch der Konstitution und der physikalischen, chemischen und technischen Eigenschaften der Metalle und metallischen Legierungen, von DR W GUERTLER Privatdozent an der Konigl. Technischen Hochschule zu Berlin Erster Band Die Konstitution Heft 7- 12, pp. i-lv, 449 1177. Berlin, Verlag von Gebruder Borntrager

In these volumes, which have appeared from time to time during the past year the author brings to a conclusion the first volume of his treatise on the constitution of the metals and their alloys. He has proceeded in the same orderly manner and has discussed critically and with great thoroughness the equilibrium diagrams of all those metals not treated in the first six parts (Review, THIS JOURNAL, 35, 221). In undertaking such an enormous task the author is to be congratulated on making such excellent progress. It is natural that some parts of the work may not contain the last word, as is the case with the brasses but in a subject which is developing so rapidly this is to be expected.

Heft 7 concludes the zinc alloys, considerable discussion being given to the brasses and to the alloys of zinc with Ag, Au and the platinum group of metals. The alloys of Cd with Cr, Mn, Fe, Co and Ni and with Ag, Au and the platinum group are discussed; also the amalgams of the group Cr, Mn, Fe, Co, Ni, and Cu, Ag, Au and the platinum group.

In Chapter IX, the author discusses the binary alloys of the group Tl, Pb, Bi with each other and with members of the group Hg, Cd, Zn and Mg; and in Chapters X-XII, the commercially important group of alloys of Pb, Sn and Sb with the other metals. The interesting group of alloys of As, P, Te, Se, and S with the metals is treated in Chapters XIII-XVII. It is much to be regretted that the author decided not to include with this group the oxides.

Heft 12 is devoted to a table of contents, a most satisfactory index with many cross references, and a general index of all systems, classified by the symbols of the elements. HENRY FAY.

Quantitative Chemical Analysis. By CHARLES M. ALLEN, Head of Department of Chemistry, Pratt Institute, Brooklyn, New York. (One of a series of "Loose Leaf Laboratory Manuals" edited by J. M. JAMESON, Pratt Institute.) New York: John Wiley & Sons, Inc. Copyright, 1913. Paper covers, 21 × 26 cm.

In paper covers and bound together by a couple of paper fasteners, we have here directions for some thirteen exercises in quantitative analysis accompanied by a like number of sheets of test questions and problems to correspond. Each set of directions consists of perhaps 5 or 6 pages, and each set of exercises thereon of perhaps 1 or 2 pages, bringing the number of pages in the example before us to about 86. The publishers announce that "single pamphlets and problem sheets are furnished if desired," and point out that the size of the sheets is the same as that of an ordinary typewritten page; so that any teacher is at liberty to synthesize from these printed and from his own typewritten sheets, collected within an ordinary notebook cover, as heterogeneous and flexible a manual as he may wish, including nothing extraneous to the work of his own course. This idea has certainly some points to recommend it.

The titles of the "pamphlets" are these: general processes of gravimetric analysis, analysis of barium chloride, of magnesium sulfate, of potash alum, of limestone, general processes of volumetric analysis, analysis of acids and alkalis, of hardness in water, of iron ore, of chlorine in bleaching powders, determination of oxidizing power of pyrolusite, of sulfur dioxide in sulfite and also of hydrogen peroxide. The publishers state that other analyses are in preparation.

There are those of us who are greater purists in terminology, and who make more of a fetish of high accuracy even with beginners; but both directions and test questions are very clear and practical; they are well printed and well illustrated, upon a serviceable paper; and their teachable character is likely to commend itself to many. ALAN W. C. MENZIES.

Quantitative Analysis in Practice. An Introductory Course Designed for Colleges and Universities. By JOHN WADDELL, Ph.D., Assistant Professor of Chemistry, School of Mining (Queen's University), Kingston, Canada. P. Blakiston's Son & Co., Philadelphia, 1913. 162 pp. Price, $1.25 net.

The book contains 36 pages of well written preliminary discussion, followed by 24 pages of directions for the analysis of pure salts ($BaCl_2.2H_2O$, $MgSO_4.7H_2O$, and $CaCO_3$). Then follow 84 pages devoted to rapid methods of an industrial character (Cement, Limestone, Clay; Coal; Copper; Alkalimetry; Bleaching Powder; Iron Ore; Water; Iron and Steel; Lead Ore; Nickel and Cobalt Ore; Zinc Ore; Bronze). A prominent feature is the attempt to give the student some idea of the time required for the various analyses. The remaining pages contain appendices on the Balance and Weights, Calibration of Measuring Vessels, Electrolytic

Dissociation and the Mass Law, Analytical Factors, Logarithms, and an Index.

The directions in the book are clear and concise, and with very few exceptions (*e. g.*, Nickel and Cobalt Ore) the methods are well chosen. Those who believe in this character of work for an introductory course will doubtless find the book eminently satisfactory. G. McP. SMITH.

Der heutige Stand der Synthese von Pflanzenalkaloiden. By H. BAUER. Friedrich Vieweg und Sohn in Braunschweig. viii + 144 pp. Price, bound, 5 Mark 20 Pf.

This booklet is the fifty-first volume of a collection of works on special subjects from natural science and mathematics, published under the title "Die Wissenschaft." The first eight pages are devoted to the history, distribution and general physical and chemical properties of the alkaloids, and include Pictet's hypothesis of the origin and chemism of the plant bases, together with a table of the color reactions of the more important representatives of this group of compounds. In the following eight pages those reactions are discussed which are of especial value in clearing up the constitution of alkaloids. The reactions mentioned are: saponification, hydrolysis, distillation with zinc dust, fusion with alkali, detection and determination of CH_3O and CH_3N, determination of the function of oxygen, oxidation and exhaustive methylation. The alkaloids whose synthesis has been realized are divided into five groups: pyridine, tropane, isoquinoline, purine, and hydroxyphenylalkylamine bases. In the sixth chapter the mutual transformation of certain alkaloids is described, and the last chapter treats of the syntheses of such substances as are obtained in the decomposition of some alkaloids.

The treatment of the subject, while, brief, is very clear, and each synthesis is supplied with a full list of references to original literature. The workmanship of the book is good, and the price very low.

The size of the book gives only an inadequate idea of the value of its contents. The book should be in the library of every chemist interested in this medicinally and technically important group of natural products.

H. M. GORDIN.

Weitere Beitraege zur Behandlung der Nephritis und verwandter Erscheinungen. VON MARTIN H. FISCHER. Sonderabdruck aus Kolloidchemische Beihefte, Band IV. Dresden und Leipzig, 1913. Theodor Steinkopff. 70 pp. Mk. 3.60.

This is one of a series of monographs which have appeared as supplements to *Kolloid-Zeitschrift*. It presents a discussion of the treatment of nephritis from the standpoint of the author's theory concerning the colloidal changes in the kidney which occur in this pathological condition. As nephritis is held to be a consequence of an acid intoxication the treatment is essentially a chemical one, consisting mainly in the injection of a hypertonic salt solution containing sodium carbonate. The theory and the practice of the method are fully described, and a considerable list of cases is referred to for illustration and proof. J. H. LONG.

F. Löhnis, Vorlesungen über landwirtschaftliche Bakteriologie & Gebrüder Borntraeger. Berlin. pp viii — 398. Price, $1 14.

In writing his "Vorlesungen," the author was avowedly guided by the wish to prepare a volume that would be serviceable, not only as a textbook for schools of college and university grade, but also as a ready reference book for the technically trained reader. That he has admirably succeeded in his purpose is indicated even by a superficial study of the book. Dr. Löhnis has brought together and presented in a very readable form the important facts of agricultural bacteriology. His treatment of the subject matter shows familiarity with almost everything of importance published of late in this rapidly expanding branch of bacteriology. The author is to be commended also for his lucidity of treatment and his skill in selecting references in support of his conclusions. While bearing in mind the broad principles on which agricultural bacteriology has developed, he is not indifferent to the applied phase of the subject. He tells us that, "the practical value of agricultural bacteriology lies mainly in the fact that it teaches the farmer how to make use of bacteria and molds in a manner most likely to assure success."

There are those who will disagree with the author as to the scope of agricultural bacteriology. He would exclude from this field, the microorganisms known to be pathogenic to plants, and he would pass in silence bacteria found in the water supplies in rural districts. American bacteriologists are often inclined to include a discussion of these organisms in treatises on agricultural bacteriology.

The first fourteen chapters of the book (pp. 1-212), constitute its "general" part and deal with the morphology and physiology of microorganisms. The important divisions of this portion of the book include the form, structure, development and classification of microörganisms; the life processes of microörganisms; the culture and suppression of microorganisms; and the physical and chemical changes produced by microorganisms. The remaining eleven chapters constitute the "special part." The special part is given over to a discussion of the bacteriology of foods and dairy products, and of the bacteriology of manure and soil.

The book is remarkably free from typographical errors, and from the standpoint of craftsmanship is a credit to the publishers.

JACOB G. LIPMAN.

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THE CRITICAL POINT, AND THE SIGNIFICANCE OF THE QUANTITY *b* IN THE EQUATION OF VAN DER WAALS.[1]

BY THEODORE W RICHARDS.

Received January 26, 1914.

The equation of van der Waals has excited wide interest and received well-deserved recognition on all sides for over thirty years. The genius of this great Hollander emphasized, for the first time, the important effect upon the volume of a gas probably caused by the cohesive tendency of the molecules, and pointed out that, when this tendency is taken into account, the earlier equation of Budde for hydrogen (namely, $p(v - b) = n\mathrm{RT}$) may be extended so as to apply fairly well to other gases.

The well known equation thus modified—namely, $(p + a/v^2)(v - b) = n\mathrm{RT}$—is widely used, although its limitations and its lack of exact fulfilment are generally recognized. That it is not merely an abstract mathematical formula, but is also concretely if somewhat vaguely concerned with the most important influences determining the volume of a gas, will probably be admitted by most physical chemists. Therefore the significance of its terms is a matter of interest and importance. The present paper concerns the meaning of the quantity *b*, or "co-volume"—the rather small quantity which must be subtracted from the volume of a gas in order that the remainder may correspond reasonably well with the requirements of the gas-law. The treatment of this topic will be essentially non-mathematical, partly because the situation seems at present too complex for really precise mathematical treatment. It is hoped that the discussion which follows will be comprehensible both to mathematical and to non-mathematical readers.

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[1] A preliminary treatment of this subject was given in a course of Lowell lectures in Boston in 1908, and again presented in a paper read at the meeting of the Eighth International Congress of Applied Chemistry, at New York, in September, 1912.

In an attempt at interpretation of this kind, the first step is to study the behavior of the given quantity under changing conditions. Although *b* is often assumed to be constant, much evidence is at hand which seems to prove that it probably varies under varying conditions. This possibility was suggested by van der Waals in his first paper long ago,[1] but the inference was complicated by the fact that the calculated value for *b* depends upon that assumed for *a*, and the change in the values of *b* seemed to be no greater than might have been due to uncertainty in this assumption. Hence physical chemists as a rule have been content to assume constancy in both *a* and *b*.

About fourteen years ago a few tentative unpublished calculations seemed to show me distinctly that *b* really varies, and these calculations drew my attention again to the original paper by van der Waals. They formed indeed the first clue which called to my notice the probable compressibility of atoms, and the outcome was summed up very briefly in the third item of the summary in the second paper concerning the significance of changing atomic volume,[2] as follows:

"3. That it (*i. e.*, the theory of compressible atoms) is able to interpret the actual deviations from the gas laws better than any other theory, retaining the essential import of the equation of van der Waals and modifying this equation only as regards the changeability of *a* and *b*." After thoughtful consideration of the whole subject for twelve years, I hope to explain the main idea somewhat more fully in the present communication, which does not pretend to be a final treatment of the matter.

Let us review here typical figures taken from the first paper of van der Waals.[3] First may be given a brief table showing the change of *b* (in the case of carbon dioxide) with temperature. In this table *b* is expressed first as a fraction of the total volume at 0° under one atmosphere's pressure calculated upon the assumption that $a = 0.00874$, and then in cubic centimeters in a gram-molecule of gas.

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[1] Van der Waals, "Over de Continuiteit van den Gas en Vloeistoftoestand," p. 77 (Leiden, 1873, translated by Roth, p 81 (Leipzig, 1881)).

[2] *Proc. Am. Acad.*, 37, 409 (1902); *Z. physik Chem* , 40, 607 (1902).

[3] See pp. 81, 85, and 86 of the German translation, 77 of the original Dutch already quoted.

THE EFFECT OF TEMPERATURE ON *b*.

Temperature.	*b* if *v* at 0° and 760 mm. = 1.0000.	*b* in cc. per mol.
0°	0.0023	51
13°	0.0024	53
34°	0.0026	58
50°	0.0027	60
100°	0.0029	64

Evidently *b* seems to change distinctly with the temperature, increasing as the temperature rises. Similar figures are given in the same paper for nitrous oxide and ethylene, from which it is seen that these two gases also have slight but somewhat less strongly marked positive temperature coefficients for *b*.

But, although the consistency of these results makes them mutually confirmatory, it is still undeniably the case that all the figures depend upon the values chosen for *a*; a change in this other "constant" might have led to a different conclusion about the changeability of *b*. Hence another confirmation is welcome; that, namely, to be obtained by studying the effect of pressure upon *b*, a proceeding which subjects the variability of the quantity *a* to a searching test. The following table contains the appropriate figures.

THE EFFECT OF PRESSURE ON *b* (32.5°).

v at 32.5° if *v* at 0° C and 760 mm. = 1.00	*b* if *v* at 0° C and 760 mm. = 1.000	*b* in cc. mol
1.130	(0.00255)	57
0.013	0.00251	56
0.0080	0.00254	57
0.0072	0.00252	56
0.0070	0.00251	56
0.0063	0.00248	55
0.00427[1]		
0.0038	0.00216	48
0.0032	0.00199	44
0.0029	0.00190	42

Thus *b* seems to remain essentially constant over a wide range of pressures, but suddenly begins to diminish when very high pressures and very small volumes are attained. The constancy of *b* under low pressures seems to indicate at least that if *a* and *b* vary, their variations must exactly counterbalance. There is no evident reason why *b* should change over a wide range of pressure until one reaches the neighborhood of the bulk of *b* itself, whether the molecules are compressible or not. On the other hand, the sudden decrease of *b* under high pressures (when the volume of the gas has been brought almost down to the bulk of *b* itself) may indicate that then the entity represented by b is really being compressed. It is perhaps not an accident that the bulk at which this compression begins to be manifest is about the critical volume, as will be shown later.

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[1] This is the critical volume. The density of carbon dioxide at the critical point (31.35°) is 0.464 (Amagat, *Compt. rend*, 114, 1093 (1892)). Keesom found 0.0042 to 0.0044 according to the method used. See his thesis for doctorate, Amsterdam, 1904.

Van der Waals, returning to this subject after more than a quarter of a century,[1] came to the conclusion that his old value for a might be somewhat too large—the more accurate value seeming to be nearer 0.0085 than 0.00874; and his further calculations, while too complicated to review here, led him to think that the expansion of b with temperature was less and the compression of b at high pressures was greater than he had supposed at first. Although the usual value for b seemed to be as large as 0.0023, the smallest possible value of b under great pressure might be as small as 0.0007—only one-third of the value usually credited to this so-called constant. It matters little here which alternative is chosen. Although the situation is by no means clear, and van der Waals himself was evidently puzzled by some of the results of his own calculations, one leaves the perusal of his paper with a feeling of agreement with van der Waals' own conclusion that whatever reasonable value one may choose for a, the value of b must be assumed to shrink under very high pressures, and to change slightly with increasing temperatures. Moreover, besides van der Waals, many others, especially Ramsay and Young, have furnished further considerations which may be interpreted to signify the changeability of b.[2] Van der Waals suggested tentatively (on p. 284, *l. c.*) that the assumption of molecular compressibility might help in the explanation, but neither he or any other seems to have carried this idea to its logical conclusion.

In almost all cases the value assigned to b depends essentially (as in the case above) upon the value chosen for a. Because even the constancy of b over a large range of moderate pressures affords no certain criterion as to whether or not the choice is correctly made, it is manifestly desirable that we should obtain, if possible, data free from dependence upon the affinity-constant. Fortunately there exist two elementary substances, hydrogen and helium, having values of a so unusually small that as a first approximation this quantity may be considered as wholly negligible in the gases under atmospheric pressure. These elementary gases ought, therefore, to afford valuable and interesting information bearing upon the present problem, and their evidence is especially significant because the former of these gases contains two atoms to the molecule and the latter only one. The comparison of the two, then, ought not only to tell us whether b changes with the temperature, but also to decide whether this change is entirely a question of the space between the atomic centers in the molecule, or whether the atoms themselves are compressed. If helium exhibits a change of b with the temperature, we cannot but think that its atom may actually be changed in volume by changing conditions.

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[1] Van der Waals, *Z. physik. Chem.*, 38, 257 (1901). See also *Chem. Weekblad*, 10, 624; reviewed in *C. A.*, 8, 598 (1914).

[2] Ramsay and Young, *Phil. Mag.*, p. 196 (1887).

Fortunately modern accurate data exist both for hydrogen and helium.[1] From among the wealth of available figures, in order to eliminate a change in a as much as possible from consideration, the value of b should evidently be calculated from the results obtained under comparatively small pressures and at temperatures not too low, so that the volume of the gas shall be fairly large and the term a/v^2, shall be as small as possible. The following table contains comparable results at 0° and 100° for both helium and hydrogen. The actual value of pv for 0° and atmospheric pressure is taken as equal exactly to unity.

TABLE I.—HELIUM

Temperature.	p.	pv.
0°	1	1.0000
	26.634	1.0139
100.35°	1	1.3674
	42.574	1.3873
	Hydrogen	
0°	1	1.0000
	30.00	1.0181
100°	1	1.3661
	30.00	1.3858

From these figures (on the assumption that a in each case is so small as to be negligible when v exceeds 0.7 liter per mol) the value of b is easily calculated with close approximation from the equation of Budde: $p'(v'-b) = RT = p(v-b)$; whence $b = (pv - \mathrm{RT})/p$; or $b = (p'v' - pv)/(p' - p)$. The resulting values are given in the following table.[2]

TABLE II.

Values for b for helium and hydrogen.

(Expressed in terms of cubic centimeters per mol of gas.)

Temperature.	Hydrogen.	Helium.
100°	15.1	10.4
0°	13.8	12.0

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[1] Hydrogen.—Witkowski, *Krak. Anz.*, **1905**, 305–338. Helium—Kamerlingh-Onnes, *Proc. Sci. Akad. Amsterdam*, Jan. 23 (1908), p. 448, March 28, 1908, p. 741–742; Comm. Leiden, number 102*a*.

[2] If a is not so small as to be negligible, the result of this calculation is, of course, not b, but a virial of the approximate form $b - a/pv$. For hydrogen and helium over ordinary low pressure and high-temperature ranges this may be taken numerically as $b - a/\mathrm{RT}$ without important error. Thus if a is thought to be large in these gases, b with helium must be conceded to possess an even greater increase with falling temperature than that indicated above; and in the case of hydrogen the temperature-coefficient of b may become negative, like helium. If with hydrogen a is assumed to exceed

The interesting and striking point about these figures is that, whereas with rising temperature the value of b for hydrogen increases, the value of b for helium decreases. Perhaps, it is true, one might ascribe these small differences to error of experiment, but the consistency of the figures for hydrogen at even higher pressures leads one to believe that the experimental error is much smaller than these[1]. Calculated in the same way the value of b for hydrogen between 30 and 60 atmospheres is 15.2 at 100° and 14.2 at 0°, agreeing reasonably well with the values given in the table for much lower pressures. In the case of helium, it is true, the results at higher pressures do not seem to be quite so consistent. If we take the extreme range of pressure studied by Kamerlingh-Onnes (about 50 atmospheres at 0° and 66 atmospheres at 100°) the results are 10.8 at 100° and 11.5 at 0°. Although the difference is less between these figures than between those for the lower pressures given in the table,[2] the qualitative conclusion is the same; the value of b seems to decrease as the temperature rises, instead of increasing as in the case of hydrogen.

The most probable explanation for the opposite characters of the two gases is not far to seek. Let us consider first the case of helium. The quantity b is generally admitted to be a function of the bulk of the molecules themselves, therefore changes in b must be referred back to changes in this bulk. Thus, from the table above, when the molecules of a gas are single isolated atoms, their available bulk seems to decrease with rising temperature. Since we must look upon b as a function of some-

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0.0002, b will exceed 0.0008 (or 18 cc. per mol) and its temperature-coefficient will become negative. Since this paper was sent to the press Mr. R. H. Kent, of the Physics Department of Harvard University, has kindly brought to my notice strong evidence, worked out mathematically but not yet published by him, tending to show that this is really the case with hydrogen and argon, and probably also with carbon dioxide and many other gases. This conclusion intensifies the argument of the present paper. Nevertheless, for the present, I prefer to leave my original statements as they stand, accepting the usual values given to a and b, because then there is no risk of exaggerating the evidence. It is enough for the present argument that a single gas should show a definite decrease of b with rising temperature. No assumption whatever with regard to the value of a can change this conclusion. The question as to whether the others have a positive or negative temperature-coefficient is merely a question as to whether the positive or negative effect (each of which must be present) happens to predominate. Incidentally, the appearance of a positive plug-effect with hydrogen may perhaps be explained, in part, by the inherent distending tendency of atoms now under discussion; in most gases, of course, it must be supposed to be hidden and masked by the greater negative plug-effect due to cohesion.

[1] The excellent data of Kamerlingh-Onnes for hydrogen lead to the same conclusion. *Proc. Sci. Kon. Akad Wetensch. Amsterdam* X[2], 420 (1908).

[2] The reason for the disagreement is not easy to find. At low temperatures, too, helium is irregular. It is possible that helium has a tendency to form double molecules under high pressure and at low temperatures. The singular maximum in its liquid density at 2.2° absolute (Kamerlingh-Onnes) points in this direction.

thing which may be termed the "effective collision-bulk" of the molecules, does not this contraction with rising temperature signify that isolated atoms of helium are more compressed by collision, the greater the kinetic energy of the moving molecules? It would be highly desirable to verify this tentative conclusion with other gases, but unfortunately all other monatomic gases have large values for a.[1]

The quite different case, illustrated by hydrogen and carbon dioxide, is equally easy to explain upon the same basis; and probably most other substances fit into this latter category, since most other substances have polyatomic molecules. Here the coefficient of expansion of b is positive, or at any rate (even if we imagine that a and b are both decidedly larger than here assumed) distinctly less markedly negative than in the case of helium. Is it not likely that two opposing effects occur in these polyatomic molecules? Increased compression on impact with increasing temperature must be supposed to occur in hydrogen as well as in helium, but the effect is concealed, because, at the same time, the centers of the atoms in any given molecule are probably separated more widely, as the temperature rises, by the rotation of the diatomic molecule—which may affect the apparent size. Thus these two effects, the decrease in effective collision-bulk of the atom due to more violent impact, and the increase due to the expanded rotating state of the molecule, seem almost to balance one another, the latter slightly predominating if a is small.

The conclusion that atoms, when free and uncombined as in helium, expand but little, if at all, as the temperature rises, is entirely in harmony with the well known tenet of the kinetic theory of gases that all the heat-energy of a monatomic gas is translational and none of it is internal. The apparent expansion of the hydrogen molecule with heat is equally in accord with this theory, because the increased specific heat of hydrogen, and of other gases with polyatomic molecules, points to consumption of energy within the molecule in rotation, as usually assumed, or otherwise.

Thus the evidence is very strong and very consistent that b changes with changing conditions, and the most reasonable explanation of the facts seems to indicate that not only the molecules but also the atoms themselves are compressible.

If, then, molecules are capable of changing their volume under changing conditions, and are deformed or distorted during the violent impact caused by their mutual collisions when flying about in a confined space, one inevitably infers further that *time* must be consumed in the act of collision.

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[1] Compare Stefan (*Wiener Sitz. ber.*, 45, *Abth.*, 2, 339 (1872); also O. E. Meyer (Baynes) "Kinetic Theory," p. 166 (1899). Stefan imagined a compressible environment, but still conceived of the imaginary hard core.

The relation of this time spent in collision to that required in flight over the mean free path between collisions is an important item to be considered. The mean free path of hydrogen under ordinary conditions has been calculated to be as much as 0.000185 mm. whereas the diameter of the hydrogen molecule is supposed to be not much over 0.0000001 mm., an amount less than 0.1 of 1% of the free path. This being the case, the time spent in collision, even if the molecule were considerably deformed by the force of the impact, could hardly be a very important percentage of the whole time, although the deformation might correspond to a very appreciable percentage of the diameter of the atom. For the present discussion it is important to note that the time of collision is probably the same, no matter what the temperature may be, for the time spent in the actual collision of an elastic ball with an elastic barrier is independent of the velocity of the striking ball. This being the case, the figures just mentioned, especially those for helium, which are more simply interpreted, must refer to a real increase in compression in the atom as the temperature rises, because the falling off of *b* could not be ascribed to any increase of time of impact.

Several months before van der Waals' above-mentioned paper[1] had appeared, I tentatively brought forward a number of arguments of quite different sort, indicating that atoms (and therefore molecules) may well be supposed to be compressible; and the data pointing in this direction have multiplied greatly during the last ten years.[2] In the most recent work at the highest pressures as yet attained in accurate experiments on compressibility, Bridgman admits that atoms must probably be imagined to be compressible, in order to explain his results.[1] Hence there is now a great bulk of testimony which is irreconcilable with the early assumption of van der Waals that molecules are incompressible and that the rebound after a collision between them is truly instantaneous.

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[1] Van der Waals, *Z. physik. Chem.*, 38, 283 (1901).

[2] Following are the titles of the several recent papers bearing upon the theory of compressible atoms with references:

"The Possible Significance of Changing Atomic Volume," *Proc. Am. Acad.*, 37, 1 (1901); *Z. physik. Chem.*, 40, 169 (1902); *Chem. News*, 86, 81 (1902).

"The Significance of Changing Atomic Volume. II. The Probable Source of the Heat of Chemical Combination and a New Atomic Hypothesis," *Proc. Am. Acad.*, 37, 399 (1902); *Z. physik. Chem.*, 40, 597 (1902).

"The Significance of Changing Atomic Volume. III. The Relation of Changing Heat Capacity to Change of Free Energy, Heat of Reaction, Change of Volume and Chemical Affinity," *Proc. Am. Acad.*, 38, 293 (1902); *Z. physik. Chem.*, 42, 129 (1902).

"New Method of Determining Compressibility, with Application to Bromine, Iodine, Chloroform, Bromoform, Carbon Tetrachloride, Phosphorus, Water and Glass," THIS JOURNAL, 26, 399 (1904); *Z. physik. Chem.*, 49, 1 (1904)

"The Significance of Changing Atomic Volume. IV. The Effects of Chemical and Cohesive Internal Pressure," *Proc. Am. Acad.*, 39, 581 (1904); *Z. physik. Chem.*, 49, 15 (1904).

"The Relation of the Hypothesis of Compressible Atoms to Electrochemistry," *Trans. Internat. Electr. Congress*, 2, 7 (1905).

"Densities of Lithium, Sodium, Potassium, Rubidium, and Caesium," THIS JOURNAL, 29, 117 (1907).

"The Compressibility of Lithium, Sodium, Potassium, Rubidium, and Caesium," *Publ. Carnegie Inst. Wash.*, 76, 9 (1907); *Z. physik. Chem.*, 61, 77 (1907).

"The Compressibility of Carbon, Silicon, Phosphorus, Sulfur, and Selenium,"

In thus describing atoms as compressible I do not mean to make any assumption whatever with regard to the mode of distribution of their "substance" (whatever that may be) within their boundaries. I mean merely to declare that there seems to be a distending tendency in each atom, entirely different from and unconnected with the vibration of heat, and that this distending tendency seems to have a fairly well-marked boundary which is compressed by the application of pressure. Heat seems to distend this boundary only when atoms are combined chemically or cohesively with other atoms. It may be, of course, that the atom, as Larmor and others have suggested, is a vacuous space in an extremely dense ether. If so, this boundary must be supposed to be the boundary of that vacuous space. Again, the idea of atomic compressibility is quite combatible with the recent hypothesis which postulates a composite structure containing electrons. Many other suppositions might also comply with the requirements, but so far as I can see there is nothing in any of the facts demanding the assumption of the small, hard, incompressible core which has been the subject of so much speculation and often fruitless mathematical analysis in the past.

Publ. Carnegie Inst. Wash., **76**, 29 (1907); *Z. physik. Chem*, **61**, 77 (1907).

"The Linear Compressibility of Copper and Iron, and the Cubic Compressibility of Mercury," *Publ. Carnegie Inst Wash.*, **76**, 44 (1907); *Z. physik. Chem.*, **61**, 183 (1907).

"The Compressibilities of the more Important Solid Elements and their Periodic Relations," *Publ. Carnegie Inst Wash.*, **76**, 56 (1907); *Z physik. Chem.*, **61**, 183 (1907).

"The Compressibilities of the Elements and their Periodic Relations," THIS JOURNAL, **31**, 154 (1909).

"The Compressibilities of the Chlorides, Bromides, and Iodides of Sodium, Potassium, Silver, and Thallium," THIS JOURNAL, **31**, 158 (1909); *Z. physik. Chem*, **71**, 152 (1910).

"The Fundamental Properties of the Elements," Faraday Lecture, *J Chem. Soc.*, **100**, 1201 (1911); *Science, N. S.*, **34**, 537 (1911); *Proc. Chem Soc.*, **27**, 177 (1911); *Revue scientifique*, **50**, 321 (1912); Smithsonian Report, p. 199 (1912).

"Compressibilities of Certain Hydrocarbons, Alcohols, Esters, Amines, and Organic Halides," THIS JOURNAL, **34**, 971 (1912).

"Die Bestimmung der Kompressibilität flüssiger und fester Substanzen.," Handbuch der Arbeitsmethoden in der anorganischen Chemie., p. 247, Leipzig, 1912

"The Chemical Significance of Crystalline Form," THIS JOURNAL, **34**, 381 (1913).

"The Theory of Compressible Atoms," *Harvard Graduates' Magazine*, **21**, 595 (1913).

[1] Bridgman, *Proc. Am. Acad.*, **47**, 549 (1912).

Most, if not all, other investigators seem to have overlooked a very simple means of testing whether or not molecules and atoms (as conceived by van der Waals) are held apart merely by the vibration of heat, as most people suppose. If this were the case, the particles should lie closely packed when all heat is removed from a body, because then the vibration is supposed to cease. Therefore, the smallest possible bulk which molecules could be made to occupy might be inferred from their bulk at the absolute zero, upon the assumption that no kinetic energy remains at that temperature. Let us take the case of mercury, which is especially suitable for discussion, because of its monatomic nature. The volume of a gram atom of mercury at its boiling point, 357°, is 15.7 cc. At —39° when solid, its volume is 14.1 cc.; at —188° it is 13.9. Extrapolating linearly to the absolute zero, the value is found there to be not less than 13.8. The total decrease in volume from the boiling point to the absolute zero is about 12%, or 1.9 cc. per gram atom; but if a system of incompressible spheres (as assumed by van der Waals) were pressed into its most closely packed assemblage, the loss of volume would be not 12 but at least 40%.[1] Evidently, then, something not indicated in the equation of van der Waals and independent of heat, prevents the atomic cores usually imagined from approaching one another.

This case of mercury is not an unique or unusual one. The same phenomenon is to be observed in most, if not all, other substances. For example, Roth has extrapolated the density of common ice to the absolute zero, and finds the molecular volume at this temperature to be 19.2. This is actually larger than the bulk of the same amount of water at its boiling point (18.8). In general the contraction of substances on cooling to the absolute zero is found to be very small. For example, Cohen and Olie[2] find that at low temperatures the density of diamond is almost independent of temperature, and graphite also has a very small temperature-coefficient. White tin falls off less than 1% in volume in going from the temperature of the room to —163°, and gray tin loses only about one-third of 1% of its volume over that range. The bulk of gray tin at the absolute zero is much greater than that of liquid tin at the highest temperatures thus far studied; for according to Day and Sosman[3] the density (6.16) of tin at 1600° C. is nearly 6% greater than that (5.75) of gray tin at —163°. It is true that tin and ice are exceptional substances, but the fact remains that in general the contraction suffered by all substances on cooling is (so far as I can discover) much less than that required by the small incompressible cores of van der Waals. Clearly the compressible

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[1] The bulk of van der Waals' molecule ($^1/_4\ b$) for mercury is taken, as usual, to be 0 3 times the volume of the liquid at the boiling point, or 4.7 cc.; and the closest packed system of small spheres occupies about 57% of the bulk of its containing vessel.

[2] *Z. physik Chem* , 71, 400 (1910)

[3] Private communication to the editors of Landolt-Bornstein's Tables, p. 168 (1912).

"sphere of influence" accompanies the atom wherever it goes; the imaginary incompressible core simply marks the limit of the compression in each particular case. The puzzling changes exhibited by this imaginary core need therefore occasion no surprise.

Let us now inquire what bearing molecular compressibility may have upon the significance of the quantity b.

At the outset we perceive the inevitable error of a familiar proposition of van der Waals, namely, that the quantity b represents four times the actual bulk of the molecules. This tenet seems to have been accepted by everyone without much question, but it loses all authority if molecules are compressible, because incompressibility of the molecules was assumed in its ingenious deduction.[1] Fairness to the brilliant Hollander demands the statement of the fact that he himself accepted his own proposition with some reserve; this is clear from his statements showing that the supposed relation cannot possibly hold in greatly compressed gases.[2]

Further study seems to suggest that the molecules really occupy much more than one-fourth of the space b. Two causes would tend to reduce the apparent size of b if the molecules are compressible. In the first place the mutual compression of two molecules on collision would make their apparent diameter during contact less than it is when each molecule is free. Secondly, the time consumed in this collision would make the centers of the molecules seem to approach even more closely to one another than they really do. From the first cause alone a diminution in the diameter of only one-third would make the bulk of the molecules appear to be almost as small as a quarter of their true bulk. Let us suppose, for a moment, that this is really the extent of compression on collision; then if b is to be taken as four times the *apparent* bulk, its magnitude calculated from these data, although quadruple the apparent size, would not be far from the actual space occupied by the molecules. Thus if one admits that the molecules are compressible, it seems easily possible that the space occupied by the molecules is really at least as large as b.

Let us review briefly the results for carbon dioxide with this in mind. From van der Waals' table on the effect of pressure, already cited, one finds that at 32.5° b remains essentially constant with decreasing volume, until the gas has been compressed to a bulk only one hundred and sixtieth of its bulk under atmospheric pressure. When this bulk is halved yet again, bringing the volume down into the neighborhood of that b, its b is seen at last to diminish. Interpreting, we may infer that as long as the molecules are fairly far apart in the gas, the volume-effect ascribed to b

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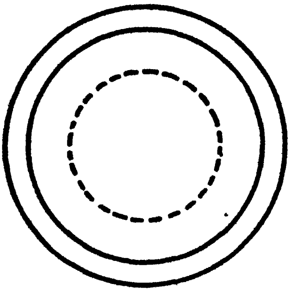
[1] Van der Waals, "Over de Continuiteit, Etc.," p. 52 (1873). This chapter was much expanded in the German translation, and the incompressibility of the molecules, at first tacitly assumed, was explicitly stated (pp. 46, 57, 59 of German translation) (1885).

[2] Van der Waals, "Die Continuiteit, Etc.," trans. by R. Roth, Leipzig, 1881, p. 55.

depends only upon single collisions, and these at a given temperature cause no more change in volume in a much compressed gas than in a comparatively rare one. On the other hand, when the bulk of the gas is reduced to the neighborhood of the bulk of the molecules themselves, these will begin to be compressed by the outside pressure, the whole situation will be changed, *a* may be supposed to increase rapidly, and the total effect of the compression will be greater than that due to collision alone. At this point, according to the theory above advocated, the pressure must be supposed to be no longer due primarily to free collisions with the walls, but rather to the above-discussed distending tendency of the atoms themselves, assisted by the infinitesimal impacts of such an elastic movement as is visible in magnified form in the Brownian movements. From the constancy of *b* down to a definite point, and its sudden decrease afterwards, one may conclude that the volume in which the molecules themselves begin to be compressed (that is to say, the critical volume) is not very far from the actual bulk of the molecules. This in the case of carbon dioxide is about 5/3 *b* at 31.35°.

The accompanying diagram is intended to show cross-sections of the three volumes under consideration, which have been imagined to occupy spheres, although of course in an irregular molecule exact spherical form can hardly be attained. The actual experimental volume of 44 grams of carbon dioxide at the critical point is 94.8 cc., and the value of *b* as calculated from the gas at the same temperature is 57 cc. One-quarter of *b* is therefore 14.25. The radii of three spheres having these relative volumes are to one another as 1.86 : 1.55 : 1, respectively, and the circles drawn with these radii give a rough idea of the relations under discussion.



In this diagram, the outermost ring indicates the actual critical volume, the next ring indicates *b* at the critical temperature, and the innermost dotted ring indicates the imaginary $^1/_4\,b$ demanded by the original hypothesis of van der Waals. The volumes are 95, 57, and 14.2 cc., respectively, per gram molecule of carbon dioxide.

Another more striking fact which supports the conclusion that the actual bulk of the molecules is greater than *b* (instead of being only one-quarter *b* as van der Waals assumed) is the well known but often overlooked fact that the quantity *b*, as computed from the behavior of a gas, is not very far from the actual volume of the liquid to be obtained from that gas.

A few data will demonstrate this nearness of the quantity *b* to the actual volume of the liquid. In the first place, the classic case of carbon dioxide may be quoted; its value of *b*, calculated at 13° from the behavior of the gas and expressed in terms of cubic centimeters per mol of gas is

53 cc. But the actual molal volume of liquid carbon dioxide at 13° is also about 53 cc.[1] Thus in the case of carbon dioxide *b* equals the actual volume of the liquid at 13°. At lower temperatures the volume of the liquid becomes less than that of *b*, at high temperatures the volume of the liquid becomes greater than *b*.

Other significant data of the same kind are not plentiful, because *b* is not often calculated as above from the behavior of the gas. This was done by van der Waals in his original paper for nitrous oxide and ethylene, but unfortunately our knowledge of the densities of these gases in a liquefied condition is not very comprehensive. The molecular values for *b* calculated by van der Waals for these two substances (about 42 and 56 cc. per gram molecule) would correspond to densities probably attained by the liquid at a boiling point under pressure greater than atmospheric pressure, but considerably below the critical pressure.

Although data for *b* obtained from the state of gas are far from plentiful, very many values for this so-called constant have been calculated from the critical data according to the equation of van der Waals. For our present purpose this procedure is unsatisfactory, for it assumes the accuracy of an equation which is really only an approximation. Moreover, in those cases where a comparison is made between the values obtained in two different ways, the values for *b* do not exactly agree. The first comprehensive collection of such data was compiled by Guye and Friedrich,[2] and a still larger collection of data is given by Landolt-Börnstein's tables.[3] As an example of the order of disagreement the case of carbon dioxide may be cited. The gas gives a molecular value for *b* between 51 and 64 according to the temperature, but the value calculated from the critical data according to van der Waals' equation is only 42.8.

Assuming, however, that the values given by van der Waals' equation are at least of the right order of magnitude, it is interesting to note that as a general rule *b* has a volume of about 1.2 times that of the liquid at the boiling point under atmospheric pressure. The parallelism of nearly all liquids in this respect has already been noticed[4] by others, although it is usually stated in another form as follows: "Assuming the actual bulk of the molecules to be one-quarter of *b*, this actual bulk is found to be almost universally three-tenths of the bulk of the liquid at the boiling point under atmospheric pressure."

Disregarding, as we have been led to do in this paper, the ill-founded assumption that $b = 4$ times the actual bulk of the molecules, the data have new interest in showing that the bulk of the liquid under pressure somewhat above the boiling point attains a value exactly equal to *b*. If we allow the inference that *b* as found from the critical point with the help of van der Waals' equation is somewhat too small, the general principle probably still holds true, although the exact form of statement may somewhat alter.

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[1] Amagat found its density at 13° to be 0.831 (see Landolt and Bornstein, 1912, p. 155).

[2] Guye and Friedrich, *Arch. sci. phys. nat.*, 9, 505–531 (1900).

[3] Landolt-Börnstein, *Physikalisch-chemische Tabellen*, fourth edition, p. 439 (1912).

[4] For example, Nernst, *Theoretische Chemie*, p. 225 (1907)

The supposition that *b* is really not far from the space actually occupied by the molecules finds its analogy in the approximate regularity found by H. N. Morse in osmotic pressures, which conform approximately to the regular rule only when the actual bulk of the dissolved substance is subtracted from the total volume.

Although these considerations undermine confidence in the ingenious mathematical deductions of van der Waals—not because of any mathematical fault but only because of his probably erroneous premise of atomic incompressibility—the essential ideas embodied in van der Waals' equation as applied to *gases* are untouched and left as probable as ever. These essential ideas are, of course; first, that the molecules in a gas occupy space and that some allowance must be made for this space; secondly, that they attract one another, and that this attraction diminishes the pressure due to the outward momentum of the particles striking the enclosing wall.

If the equation of van der Waals thus gives a plausible and still valid, if somewhat crude, conception of the nature of a gas, its application to *liquids* is far more questionable. It is especially faulty in giving no explanation whatever of the evaporation of liquids and the condensation of vapors, one of the commonest of physico-chemical equilibria. Indeed, as is well known, it demands, in the region where liquid and vapor exist together, a state of affairs which is physically impossible, indicated by the reflex curve in the familiar low-temperature isothermals.

One may well ask how it is that van der Waals' equation can apply to the critical point, if at its best it fails to explain evaporation, and if besides we must conclude that all the mathematical considerations upon which it rests need modification. As a matter of fact, however, the application of the equation to the critical point is by no means satisfactory. Even in the case of carbon dioxide it applies only very roughly—for example, it demands a critical pressure of 50 atmospheres instead of the true value 73.[1] Most physical chemists will be inclined to admit that the equation of van der Waals cannot be expected to apply exactly to very condensed material. In order to explain the partial agreement at the critical point, it is only necessary to assume that the circumstances of collision are such as to make the compressible molecule appear, through its compression, to occupy a smaller space than that which it occupied before the collision, and that this smaller space happens to be approximately that which was required by van der Waals' first erroneous assumption. It is only reasonable that this volume should appear to be constant in gases not greatly compressed, for when collisions were not too frequent, the compression produced by each individual collision would be the same, as has already been suggested.

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[1] As is well known, the calculation is as follows: $pc = a/27b^2 = 0.00874/27(0.00255)^2$. The difficulties and inconsistencies of the equation of van der Waals are interestingly reviewed in the masterly treatment of the theory, published by H. Kamerlingh-Onnes and W. H. Keesom in the Supplement 23, Volume 11, of the Communications from the Physical Laboratory of the University of Leiden. The page is numbered 799 above and 185 below. The possible compressibility of molecules is suggested not only there, but also on the page numbered 704 above and 90 below This monograph was also published by the *Encycl. der Math. Wissenschaften*, 1912, pp. 615–945, and the page numbers on the top of the separate reprint are those in the encyclopedia.

The existence of the critical point, at which it is possible to pass continuously from a state of liquid to a state of gas without any visible sign of the transition, has always been imagined to be one of the strongholds of the old theory. It was undoubtedly the approximate but perhaps accidental efficacy of the theory at this point which stimulated many to apply the kinetic theory of gases to liquids, supposing that if continuous transition exists from one to the other, the two forms of matter must necessarily be of the same structure. I shall endeavor, however, to show that this is not a necessary consequence, and that the fact of continuous transition from the liquid to the gaseous state at this particular point does not by any means necessarily fasten upon liquids and solids the same interpretation as that which applies to gases. As a matter of fact, a vapor and its liquid are not continuous under pressures below the critical pressure; and true continuity exists only at the critical point itself.

May not the critical point be explained on the basis of the hypothesis of compressible atoms as follows? A substance in the state of gas, at a temperature above its critical point, may be imagined to be gradually compressed by outside pressure until it occupies the volume which the liquid might be expected to occupy. The pressure will then be much above the critical pressure. According to the theory of compressible atoms, the spaces between the molecules would hereby be reduced to nothing, that is to say, the molecules would be packed in closely together, not only by their own attraction but also by outside pressure. If the pressure were removed, they would fly apart as a gas, because the energy of their vibration would be enough at this high temperature to overcome cohesion and to cause this effect. No sign of any liquid would be manifest. If, on the other hand, the substance were cooled, while thus compressed, to a temperature below the critical temperature, it is obvious that no change in appearance could be expected; the molecules, being already closely pressed together, could not combine into separate drops under the effect of the cooling. Each would remain in its old position, but if the pressure were now removed at this lower temperature the cohesion would be enough to withstand the diminished vibratory energy, so that a liquid would remain in the vessel. The transition would be continuous only because the molecules had been pressed so closely together by outside pressure that they could get no closer.

The critical point may obviously be supposed to be merely the dividing point between the first and the second of these alternatives. Thus, according to this explanation, the boiling point is that point at which the effect of the thermal tendency of the liquid to fly apart is exactly balanced by the sum of the effects of cohesion and vapor pressure, while the critical point is that at which, still fulfilling these conditions, the molecules in the vapor are forced by outside pressure into juxtaposition.[1]

The extreme sensitiveness of the critical point and the enormous volume-changes which take place in its vicinity, are quite in accord with this explanation. The equilibrium between an attracting or cohesive tendency (which may be supposed to grow with proximity) and a thermal disintegrating influence which is just able on the average to withstand this binding effect superposed on top of the distending effect of the compressed molecules, would naturally be a highly unstable one.

The equation of corresponding states about which much is written is not at all inconsistent with this conception of the nature of b and of the imagined mechanism of the critical phenomena. On the other hand, the present point of view provides a flexibility, lacked by preceding generalizations, which affords a reasonable explanation for the fact that the equations of van der Waals and of corresponding states are only approximate generalizations.

The immense multiplicity and variety of the published theories and facts concerning the critical point and the theory of van der Waals make it entirely impossible for any single individual to have made even a passing acquaintance with all. I have endeavored to seek information from many sources both by reading and by personal inquiry, and have sought to do justice to every earlier suggestion known to me, but some important contributions may have been overlooked. Therefore this essay is not intended in any way to claim ultimate priority with regard to any of the ideas advanced in it, although some of them may be new. The attempt has been made rather to show the modifications which seem to me to be needed in some commonly accepted notions, as well as to point out the consistency of all the facts with the theory of compressible atoms.

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[1] A briefer statement of this definition will be found in one of the earlier papers on changing atomic volume, *Proc. Am.*, 37, 409 (1902); *Z. physik. chem.*, 40, 606 (1902).

Summary.

In this paper the following facts and interpretations are set forth:

1. The value of *b* in carbon dioxide must be admitted to vary according to conditions in such a way that, although fairly constant under moderate pressures, it diminishes greatly with very high pressures.

2. The value of *b* in hydrogen and carbon dioxide is probably affected by temperature, the nature of this effect being dependent on the value assumed for *a*. Both of these probabilities seem to be accepted by van der Waals himself.

3. The value of *b* with the monatomic gas helium is found to have a decidedly negative temperature coefficient.

4. This decrease in *b* with rising temperature seems to imply that the helium atoms are compressed by collision, the greater compression taking place at high temperatures because of the greater kinetic energy of collision. This conclusion suggests further that uncombined atoms are not expanded by rise of temperature —a conclusion in keeping with the solely translatory effect of heat on monatomic gases.

5. In polyatomic molecules this effect may be supposed to be partly counteracted by some sort of expansion of the molecule due to the energy expended within the molecule, as indicated by the larger specific heat of polyatomic molecules.

6. Therefore, since *b* may be supposed to be a function of the actual size of the molecules, one is driven to conclude that molecules may change the effective size which they assume under collision.

7. If the atoms and molecules are thus compressible, van der Waals's conclusion that *b* is equal to four times the actual molecular bulk falls to the ground; one must assume that the molecules really occupy considerably more space. It is not unreasonable to imagine that the actual molecular bulk (when the molecules are not compressed by collision or cohesion) is probably even larger than *b*, perhaps about the critical volume.

8. It is pointed out that as a matter of fact *b* occupies very nearly the bulk of the corresponding liquid at a temperature somewhat above the boiling point in many cases. This again shows that in the state of gas, when not compressed by cohesion, the molecules must be somewhat larger than *b*.

9. The approximate, although often unsatisfactory, agreement of the equation of van der Waals at the critical point is perhaps less significant than usually imagined; the continuity between the liquid and the gaseous states may be supposed to exist only at the critical point.

10. The critical temperature is defined by supposing that it is the point where the kinetic energy of the molecules is just barely enough to separate them when the outside pressure is sufficient to bring on the average the molecular surfaces into contact. Therefore the critical

volume may be about the true volume of the non-cohering molecules, as stated above.

11. From these conclusions it is evident that the theory of compressible atoms affords a satisfactory explanation for the inadequacy of the equation of van der Waals and the equation of corresponding states derived from it. The latter equation would be expected to hold better than the former, because the same kinds of deviations often exist in different gases, and the method of comparison may eliminate these.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE DOUBLE SULFATES OF SAMARIUM WITH SODIUM AND AMMONIUM.

BY D. B. KEYES AND C. JAMES.

Received February 16, 1913.

The solubility curves of the sulfates of samarium, gadolinium, yttrium and ytterbium in sodium sulfate seem to be of special interest. Samarium can be looked upon as being the first element whose double sulfate with sodium sulfate is distributed between the insoluble double sulfates and the more soluble ones. The solubility curve of gadolinium sulfate in sodium sulfate should show the reasons why some writers claim that gadolinium may be separated from the yttrium earths by this process, while others state that it can be separated from the cerium earths by this very method. Yttrium, possessing the average properties of the yttrium rare earths, as far as these compounds are concerned, shows the best concentrations under which the most complete separation can be obtained.[1] The curve given by ytterbium sulfate under these conditions would indicate, very nearly, the extreme solubilities. It would also show whether a concentrated solution of sodium sulfate would leave the members of the rare earth series, possessing the highest atomic weights, in solution accompanied by smaller amounts of the other yttrium earths.

This present communication deals with the compounds formed by samarium sulfate with the sulfates of sodium and ammonium.

The pure samarium sulfate was prepared in the following manner: Samarium oxalate was ignited and the oxide dissolved in hydrochloric acid. To the cool solution there was added a little more sulfuric acid than was required to unite with the samarium present, after which the mixture was poured into a large excess of alcohol. The precipitated sulfate was filtered off, washed with alcohol and rendered anhydrous by heating. The anhydrous sulfate was dissolved in water, filtered, and the filtrate evaporated upon the steam bath. The purified salt was then dried and very finely powdered.

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[1] This has been worked out by C. James and H. C. Holden, THIS JOURNAL, 35, 559.

Samarium Sodium Sulfate.—In order to study the system samarium sulfate, sodium sulfate and water, about twenty bottles were made up of varying concentrations. One bottle was used to determine the solubility of samarium sulfate.

After rotating for a long time in a thermostat at 25°, the analysis of the liquid phase was commenced. The procedure was as follows: two samples were removed by means of a pipet, weighed and diluted to about 100 cc each. The first was acidified with hydrochloric acid and the samarium precipitated as samarium sebacate by the addition of a solution of ammonium sebacate. The precipitate was filtered off, washed and ignited to the oxide Sa_2O_3. The percentage of $Sa_2(SO_4)_3$ was then determined from the weight of oxide.

The second diluted sample was acidified with hydrochloric acid, brought to boiling, and the SO_3 precipitated by the addition of barium chloride solution. The precipitate was filtered, washed, ignited and weighed This gave the total amount of SO_3. By deducting the amount of SO_3 required for the samarium sulfate, the quantity that was combined with the sodium was then obtained.

The results of the analyses were as follows:

Serial No.	Na_2SO_4 per 100 parts of H_2O	$Sa_2(SO_4)_3$ per 100 parts of H_2O	Serial No	Na_2SO_4 per 100 parts of H_2O	$Sa_2(SO_4)_3$ per 100 parts of H_2O
1–4	0.1	2.0	13	14.71	0.010
5	0.5	0.11	14	14.47	0.000
6	1.0	0.03	15	20.02	0.012
7	6.44	0.010	16	23.42	0.012
8	7.00	0.008	17	23.68	0.018
9	9.02	0.016	18	25.93	0.015
10	10.51	0.012	19	27.40	0.011
11	11.48	0.012	[illegible]		2.05
12	13.58	0.010			

These results, which are plotted in Fig. 1, appear to indicate that there is only one double salt formed by the union of samarium sulfate with sodium sulfate.

The double compound was prepared by mixing a saturated solution of samarium sulfate with a saturated solution of sodium sulfate, and allowing the resulting solution to stand for about two days. The precipitate was filtered off, dried, ground and washed with water and alcohol.

This salt was analyzed in the following way: a 0.5 g. sample was fused in a platinum crucible with sodium potassium carbonate. The whole was dissolved in water, leaving Sa_2O_3. This was filtered, washed and ignited, and dissolved in very dilute hydrochloric acid. The chloride solution was then brought to a boil and precipitated by ammonium sebacate. The liquid was allowed to set in an oven at 90° for one hour, and then filtered. The precipitate was washed and ignited to the oxide. The

SO_4 was obtained by precipitating with barium chloride in the acidified filtrate from the Sa_2O_3.

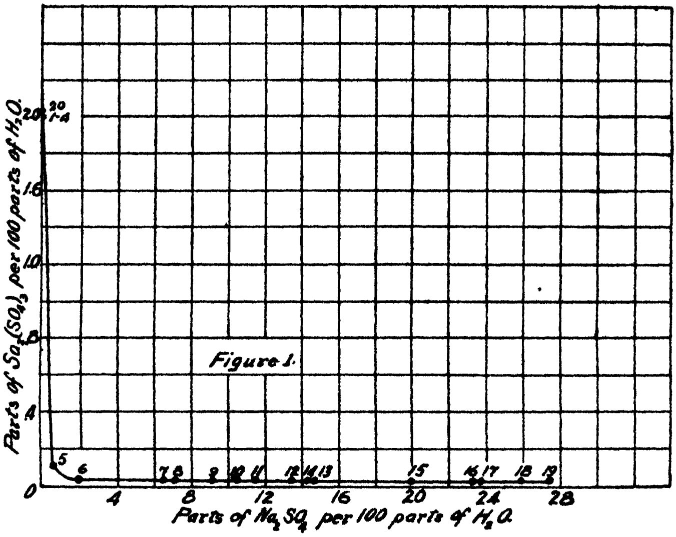

Figure 1.

Two solutions of samarium sulfate were used to prepare the double compound. One contained about 10% sodium sulfate, while the other contained about 20%.

The results of the analysis together with the ratio of molecular weights are given below.

20% SODIUM SULFATE IN SOLUTION.

	Per cent.		
$Sa_2(SO_4)_3$	67.5	0.115	2
Na_2SO_4	26.6	0.187	3
H_2O	5.9	0.330	6
$Sa_2(SO_4)_3$	68.1	0.116	2
Na_2SO_4	25.4	0.178	3
H_2O	6.6	0.366	6
$Sa_2(SO_4)_3$	66.1	0.112	2
Na_2SO_4	27.4	0.192	3
H_2O	6.5	0 362	6

Analysis of the compound formed from the 10% solution of sodium sulfate showed approximately the ratio 2-3-6, similarly to the 20% solution.

It can be seen that the results vary considerably. This is probably due to difficulties in the method of analysis. However at no time could the results, regardless of error, come to such values as to give the ratios 1-1-2, which have been accepted up to the present time.[1]

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[1] *Bull. soc. chim.*, 43, 162.

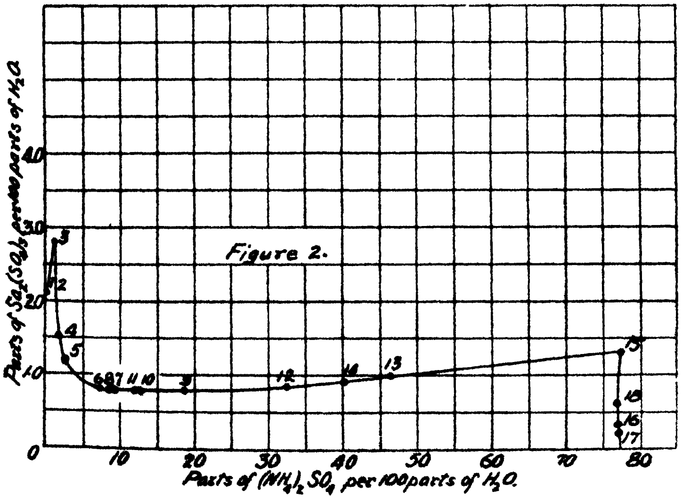
It appears, therefore, to the authors that the composition of the compound is $2Sa_2(SO_4)_3.3Na_2SO_4.6H_2O$.

Samarium Ammonium Sulfate.—Eighteen bottles of varying concentrations were made up and placed in a thermostat at 25°. After rotating for five months the solutions were found to be in equilibrium and the analysis was commenced. The procedure for the liquid phase was identical with that in the former system, with the exception that the ammonia was driven off by boiling with a slight excess of sodium hydroxide before acidifying and precipitating with barium chloride to determine the SO_3. The results of the analyses are given below.

Serial No	$Sa_2(SO_4)_3$ per 100 parts of H_2O	$(NH_4)_2SO_4$ per 100 parts of H_2O	Serial No	$Sa_2(SO_4)_3$ per 100 parts of H_2O	$(NH_4)_2SO_4$ per 100 parts of H_2O
1	2 1	0 3	10	0 8	12 2
2	2 0	0 8	11	0 8	12 3
3	2 8	1 1	12	0 9	32 5
4	1 5	1 9	13	1 0	46 3
5	1 2	2 7	14	0 9	40 3
6	0 8	7 4	15	1 3	77 5
7	0 8	9 5	16	0 2	77 2
8	0 8	8 7	17	0 3	77 3
9	0 8	18 8	18	0 6	76 8

Bottles 2, 3, 9, 11, 14 and 15 were checked and found correct.

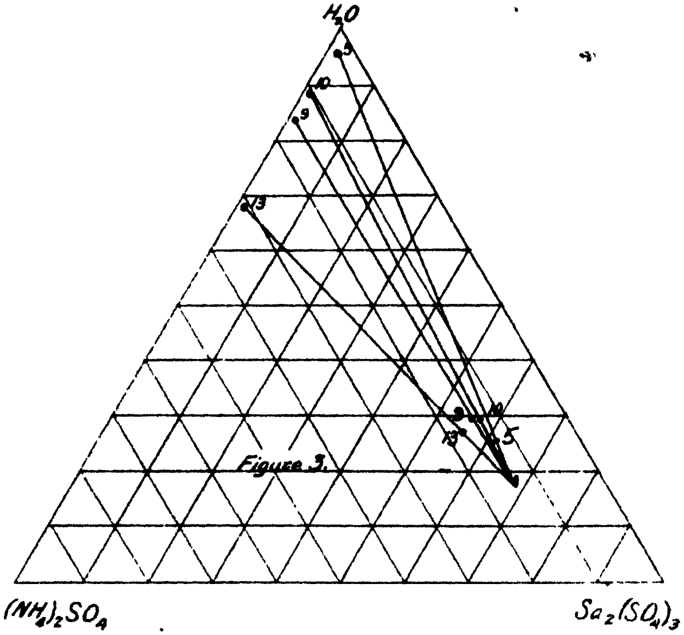
The curve shown in Fig. 2 was drawn from the above data. Along the first part of the curve (from 1 to 3) we have the solubility of samarium sulfate. From 3 to 15, the curve represents the solubility of the double compound, while from 15 on, the solubility of ammonium sulfate is represented.



The solid phase was removed from some of the bottles, and carefully analyzed, with the following results:

No.	% $Sa_2(SO_4)_3$.	% $(NH_4)_2SO_4$.	% H_2O.
5	61.7	13.0	25.3
9	55.9	15.2	28.9
10	57.0	13.7	29.3
13	55.1	17.9	27.1

From these results and from the corresponding liquid phase the triangular plot shown in Fig. 3 was made.



It will be observed that the lines intersect at a common point corresponding with the formula $Sa_2(SO_4)_3.(NH_4)_2SO_4.7H_2O$.

Some of the pure compound was prepared by washing away the ammonium sulfate from some of the solid phase from bottle 5. Analysis showed that the composition agreed well with that indicated above. This formula is similar to the one given by Cleve, with the exception of the amount of water of crystallization.[1]

DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE SEPARATION OF YTTRIUM FROM THE YTTRIUM EARTHS.

PART I.

BY H. C. HOLDEN AND C. JAMES.

Received February 16, 1914.

Although the rare earth oxides obtained from minerals such as gadolinite, fergusonite, euxinite, samarskite and xenotine carry a large percentage of yttrium, it has been found by many chemists that to obtain pure yttrium oxide involves a long and intricate process. In view of this fact, the authors have begun a systematic study of various methods in hope of finding one which will give pure material, with the greatest efficiency.

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[1] *Bull. soc. chim.*, 43, 162.

The material used in the first part of this work consisted mainly of yttrium oxide, together with some erbium oxide, the determination of the equivalent of which gave an atomic weight of 94.7. The method used in the determination of the equivalent was as follows: About 0.1500 g. of oxide was dissolved by heating in 50 cc. of carefully standardized, approximately $N/10$, sulfuric acid, after which about 8 cc. of $N/5$ potassium oxalate was added and the resulting product brought to the boiling point. This was cooled, phenolphthalein added and the excess of sulfuric acid titrated by means of approximately $N/10$ sodium hydroxide. Since the amount of acid used by the oxide was known, the equivalent could easily be determined.

(*A*) *Fractional Precipitation by Means of Hypophosphorous Acid.*—About 10 g. of the mixed oxides were dissolved in formic acid and diluted to about one liter. This solution was then boiled and stirred by means of steam, while a sufficient amount of a 5% solution of hypophosphorous acid was added to form a fair sized precipitate. The precipitate thus obtained was washed with water and dissolved in hydrochloric acid, reprecipitated with oxalic acid and ignited. On ignition, phosphine was noticed to be given off and the volume increased about three times the original. The oxide thus obtained was dissolved in hydrochloric acid and again precipitated with oxalic acid. This was washed, ignited and weighed. A portion of this was redissolved in hydrochloric acid, precipitated as oxalate, washed, ignited to constant weight and the equivalent determined. Fraction 4 was obtained from the filtrate of fraction 3 by means of oxalic acid and did not show the peculiar action on ignition of the three previous fractions. A noticeable change of color could be seen going from fraction 1, which was light pink, to fraction 4 which was nearly white.

SUMMARY.

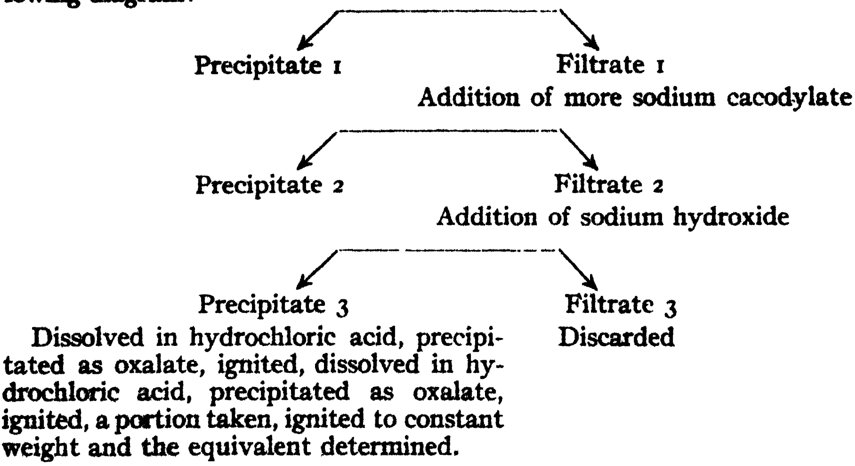
No. of fraction.	Atomic weight.	Weight of fraction.
1	96.15	2.2
2	95.20	2.0
3	93.50	2.0
4	88.30	2.5

(*B*) *Fractional Precipitation by Means of the Dimethyl Phosphates.*—Between 7 and 8 g. of the mixed oxides were dissolved in hydrochloric acid and diluted with water to about 750 cc. This was boiled and stirred as in the previous fractionations, and a dilute solution of sodium dimethyl phosphate added until sufficient precipitate was obtained for fraction 1. As the dimethyl phosphates are more soluble in cold than in hot water, the solutions had to be filtered rapidly. Three fractions were obtained in this manner. The filtrate from fraction 3 was placed in a casserole and boiled. Since an excess of sodium dimethyl phosphate was present, the remaining fractions were obtained by evaporation. The various fractions were then dissolved in hydrochloric acid and precipitated as oxalates, dried, ignited and weighed. A portion was then redissolved in hydrochloric acid, filtered, reprecipitated as oxalate, dried, ignited to constant weight and the equivalent determined. Fraction 6 was obtained by adding oxalic acid to the filtrate from fraction 5. The oxalate was ignited, dissolved in hydrochloric acid and precipitated with ammonium hydroxide. The hydroxide was filtered off, dissolved in hydrochloric acid and precipitated as the oxalate, ignited and then subjected to the same treatment as the previous fractions.

SUMMARY.

No of fraction.	Atomic weight.	Weight of fraction.
1	96.60	1.09
2	95.60	1.25
3	94.70	2.40
4	94.60	1.23
5	92.50	0.80
6	91.90	0.10

(*C*) *Fractional Precipitation by Means of the Cacodylates.*—A small quantity of the mixed oxides was dissolved in hydrochloric acid and diluted with water to about 750 cc. This was boiled and stirred as before, and a dilute solution of sodium cacodylate added until a fair sized precipitate was formed. The fractionation was then carried on as shown in the following diagram:



Precipitate 1 — Filtrate 1

Addition of more sodium cacodylate

Precipitate 2 — Filtrate 2

Addition of sodium hydroxide

Precipitate 3 — Filtrate 3

Dissolved in hydrochloric acid, precipitated as oxalate, ignited, dissolved in hydrochloric acid, precipitated as oxalate, ignited, a portion taken, ignited to constant weight and the equivalent determined.

Discarded

Precipitate 1 was dissolved in hydrochloric acid, boiled, and a 4% solution of sodium hydroxide added.

Precipitate 1A — Filtrate 1A
Addition of more sodium hydroxide

Precipitate 1B — Filtrate 1B

Precipitates 1A and 1B were then treated in the same manner as precipitate 3.

Precipitate 2 was then subjected to the same treatment as precipitate 1, 2A and 2B being obtained. These were treated as precipitate 3.

SUMMARY.

No of fraction.	Atomic weight.	Weight of fraction.
1A	96.80	2.16
1B	93.70	1.90
2A	93.70	2.70
2B	92.20	0.90
3	91.80	0.59

(*D*) *Fractional Precipitation by Means of the Phosphates.*—A small amount of the mixed oxides was dissolved in nitric acid and diluted to about 750 cc. with water, which made the solution about 1:9 concentration of nitric acid. A solution of ammonium phosphate was then prepared by nearly neutralizing a 10% solution of phosphoric acid with ammonium hydroxide. The solution of the mixed oxides was boiled and stirred as before and about 100 cc. of the ammonium phosphate added. The precipitate thus obtained was filtered, washed, dissolved in concentrated hydrochloric acid, diluted, and precipitated as the oxalate. This was then ignited, redissolved in hydrochloric acid, filtered, precipitated as the oxalate and ignited. A small amount of this oxide was taken and the equivalent determined. In a like manner, with the filtrate of the first precipitate, another fraction was obtained, purified and the equivalent determined. Fraction 3 was obtained by the same method.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	97.20	2.85
2	94.3	2.87
3	91.4	1.22

(*E*) *Fractional Precipitation by Means of the Monomethyl Phosphates.*—About 7 or 8 g. of the mixed oxides were dissolved in hydrochloric acid and water added to make the solution about 1:10 concentration of hydrochloric acid. The solution was then boiled and stirred as before and the solution of sodium monomethyl phosphate added until a fair sized precipitate appeared. This was taken as fraction 1 and from the filtrate fraction 2 was obtained in a similar manner. In this way four fractions were procured. Each fraction was then dissolved in hydrochloric acid, precipitated as the oxalate, ignited, redissolved, filtered, precipitated as the oxalate, and ignited. The equivalents were then determined, by using a small portion of each.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	96.10	2 07
2	94.9	1.83
3	93.8	0.72
4	91.7	1.44

(*F*) *Fractional Precipitation by Means of the Arsenates.*—A small amount of the mixed oxides was dissolved in nitric acid and diluted to about 750 cc. This was boiled and stirred as before and a dilute solution of sodium arsenate added until a fair sized precipitate resulted. This first precipitate was somewhat gelatinous, but the succeeding fractions grew more crystalline. Four fractions were obtained by the addition of more sodium arsenate. These were purified by dissolving in hydrochloric acid, precipitating as oxalate, and igniting, after which the equivalents were determined.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	97.4	1.56
2	95.9	0.80
3	95.8	0.84
4	91.8	2.64

(*G*) *Fractional Precipitation by Means of the Phosphites.*—A dilute solution of sodium phosphite was run into a dilute solution of the chlorides of the rare earths. The rare earth material and the method of obtaining the various fractions was similar to the method employed in the previous fractionation. The five fractions thus obtained were somewhat gelatinous, but seemed to filter very readily. They were dissolved in hydrochloric acid and precipitated as the oxalate, ignited, redissolved in hydrochloric acid, filtered, precipitated as the oxalate, and ignited. A portion of each was then taken and the equivalent determined.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	97.60	0.22
2	96.85	0.72
3	95.50	1.75
4	94.00	2.00
5	91.70	1.05

(*H*) *Fractional Precipitation by Means of the Chromates.*—A small quantity of the mixed oxides was dissolved in a solution of chromic acid and water. This was made neutral by the addition of a slight amount of oxide and then diluted with water to about 750 cc. A 10% solution of potassium chromate was added to this solution, while it was being stirred by means of steam and heated with a bunsen burner. After the addition of about 250 cc. of the potassium chromate solution, the first fraction was obtained. Three more fractions were obtained in a like manner and the filtrate from fraction 4 treated with ammonium hydroxide to obtain fraction 5. The various fractions thus obtained were dissolved in hydrochloric acid by using a slight excess, reduced by means of ethyl alcohol, boiled, and the rare earths precipitated by means of oxalic acid. These oxalates were ignited, dissolved in hydrochloric acid, filtered, oxalic acid added, the resulting oxalates ignited, and the equivalents determined.

SUMMARY

No. of fraction.	Atomic weight.	Weight of fraction.
1	103 40	0.26
2	98.00	1.60
3	96.15	0.45
4	94.20	0.90
5	89.70	1.93

(I) Fractional Precipitation by Means of the Iodates.—In this fractionation a dilute solution of potassium iodate was added slowly to a nitric acid solution of the rare earth oxides. The rare earth material and the procedure were the same as in the previous method. The five fractions thus obtained were dissolved in hydrochloric acid and oxalic acid added, which set free the iodine and also precipitated the oxalates. These were ignited, dissolved in hydrochloric acid, filtered, precipitated as oxalates, ignited, and the equivalents determined.

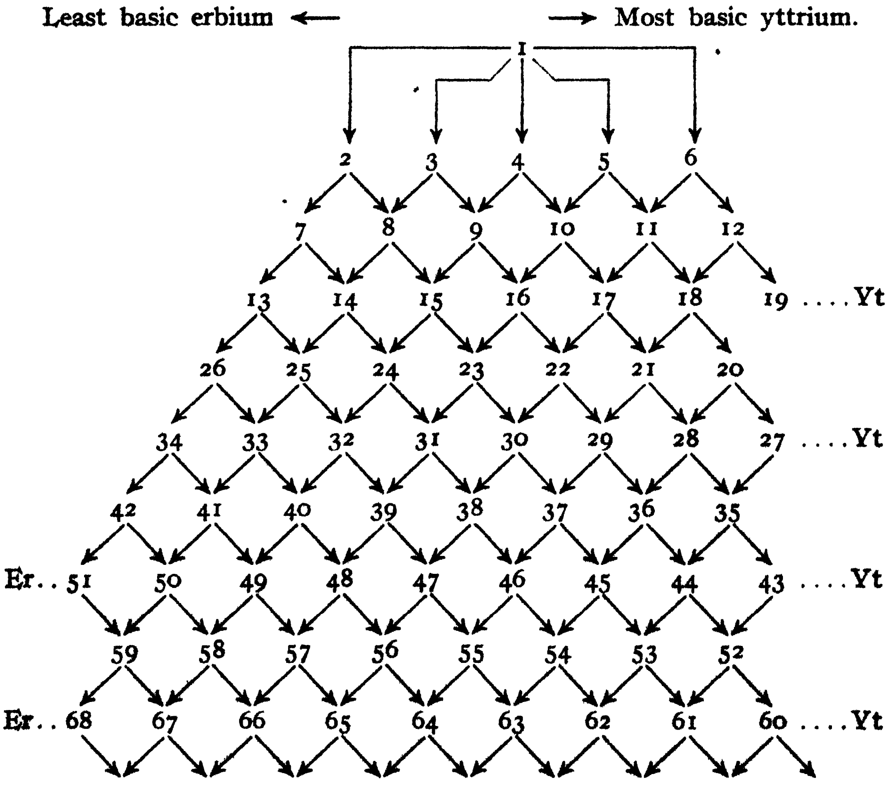
SUMMARY.

No of fraction.	Atomic weight.	Weight of fraction.
1	98.50	0.59
2	96.70	0.32
3	96.60	2.09
4	95.50	0.93
5	93.20	2.65

(J) Separation by Means of the Fractional Crystallization of the Bromates of Erbium Containing Yttrium.—The material used in conducting this work was ytterspar, euxinite, gadolinite, xenotine and fergusonite and from these, several kilograms of crude erbium bromate were obtained. This erbium bromate, containing some yttrium, was boiled with sodium hydroxide, the precipitate being filtered off and well washed with boiling water. The hydroxide was then dissolved in hydrochloric acid and the solution precipitated by means of oxalic acid. The resulting oxalate possessed an exceedingly beautiful rose tint. For separating yttrium from erbium, the method of fusing the nitrates is said to be the best. The next step was to dissolve the oxides, obtained by igniting the oxalates, in nitric acid. The solution was evaporated and the nitrates heated until brown fumes were evolved. This decomposition was allowed to proceed for a

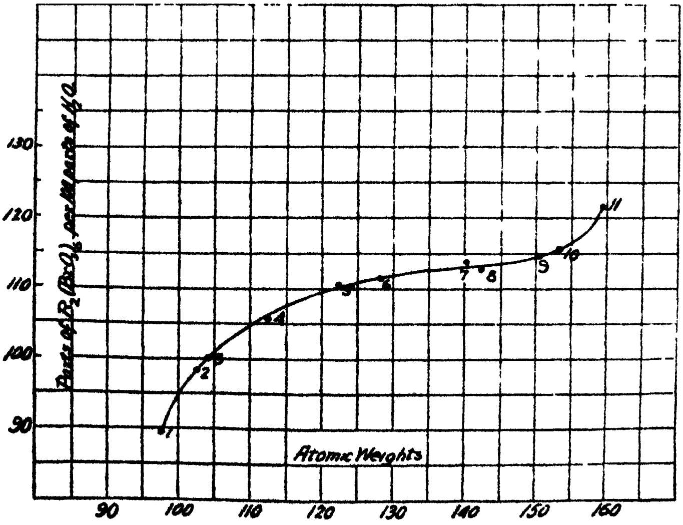
little time. When the desired period had elapsed, the "melt" was poured into an enamel iron vessel and the latter cooled by placing in cold water. The glassy nitrates were thus obtained in thin cakes which cracked into small portions and were readily removed. On boiling this product with water—the correct amount is soon judged by experience—a precipitate remained. On cooling, the solid portion increased owing to the less soluble basic nitrates crystallizing out. As erbium nitrate decomposes more readily than the corresponding salt of yttrium, the solid obtained by filtering the above is much richer in erbium than the mother liquor. The original portion was split into five fractions. The fractionation from the second series onward, was treated similarly to a fractional crystallization, *i. e.*, the mother liquor of the richest yttrium fraction was poured off, forming a new fraction while the mother liquor from the next was added to the solid remaining from the first fraction of that series and so on. After a series had been poured, nitric acid was added to each to dissolve the basic salts, after which they were evaporated to dryness and again submitted to careful fusional decomposition. These operations can be better understood from the following diagram:

FUSION OF NITRATES.


Least basic erbium ←
→ Most basic yttrium.
1
2 3 4 5 6
7 8 9 10 11 12
13 14 15 16 17 18 19 . . . . Yt
26 25 24 23 22 21 20
34 33 32 31 30 29 28 27 . . . . Yt
42 41 40 39 38 37 36 35
Er. . 51 50 49 48 47 46 45 44 43 . . . . Yt
59 58 57 56 55 54 53 52
Er. . 68 67 66 65 64 63 62 61 60 . . . . Yt

All the fractions richest in erbium were then united. This least basic portion showed the presence of scandium and ytterbium when tested in the spectrograph, and was placed on one side. The resultant fractions consisting of erbium with some yttrium were converted into the bromates and fractionated for a time. Samples were then obtained from the various fractions, placed in bottles and sufficient water added to dissolve about one half the crystals. The bottles were then carefully sealed, placed in the thermostat and rotated at 25° until equilibrium was reached. They were then allowed to stand at this temperature until the solid had settled. Samples of the supernatant liquid were withdrawn for analysis. The analysis was carried on as follows: The samples of liquid were weighed, diluted with water and oxalic acid added to free the bromine and also precipitate the oxalates of the rare earths. These were ignited and weighed. About 0.1500 g. was then taken and the equivalent determined by the method used in the previous cases. With these data the parts of $R_2(BrO_3)_6$ per 100 parts of water were determined and the following results obtained:

Bottle No.	Fraction No.	Atomic weight.	Parts of $R_2(BrO_3)_6$ per 100 parts of H_2O.
1	7	159.50	123.03
2	8	153.40	115.24
3	9	150.40	114.56
4	12	142.50	112.65
5	15	140.50	113.98
6	17	128.20	111.52
7	19	122.70	110.45
8	20	112.70	105.37
9	22	104.05	99.90
10	23	102.40	98.10
11	25	97.60	89.35



These results were then plotted as can be seen by the accompanying figure.

Conclusions.

Of all the fractional precipitational methods studied up to the present time, the chromate and phosphate show the greatest efficiency.

Fractional crystallization methods are being carried on in order to investigate the curves obtained by plotting solubilities against atomic weights.

DURHAM, N. H

NEGATIVE OSMOSE.

BY F. E. BARTELL.

Received February 5, 1914

In the usual osmotic experiments, a solution is separated from the solvent by means of a semipermeable membrane and there is produced, as a result, a flow of liquid through the membrane. The flow of the liquid, as a whole, is toward the more concentrated solution tending, thereby, to increase the volume of the more concentrated solution. This phenomenon is commonly known as osmosis; however, when referred to in this paper, it will be designated as *positive osmose.* In some of the experiments described in this paper the direction of flow of the liquid, as a whole, through the membrane is not in the direction usual in the process of osmosis but is, on the contrary, from the concentrated to the more dilute solution. This latter mentioned phenomenon will be referred to as *negative osmose.*[1]

Numerous experiments have been carried out in this laboratory in an attempt to determine the maximum size of the capillary pores in membranes with which small but definite osmotic effects can be obtained. Plain unglazed porcelain membranes and membranes of porcelain clogged with various insoluble precipitates have been investigated.[2] The main object of these experiments has been to determine the relation of pore diameter to osmotic effects produced when these different membranes are used with one and the same solute (sugar).

An attempt has been made in the present investigation to determine the relation of pore diameter to osmotic effect, when different solutes are used with one and the same grade of unglazed porcelain membranes. The value of the pore diameter of the porcelain selected was near the border line between osmotic effect and no osmotic effect for sugar solutions.

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[1] The terms positive osmose and negative osmose were used by Graham to describe similar phenomena in connection with his work on "Osmotic Force." *Phil. Trans.*, 144, 177 (1854).

[2] Bigelow and Bartell, THIS JOURNAL, 31, 1194 (1909). Bartell, *J. phys. Chem.*, 16, 318 (1912).

Apparatus and Method.

The porcelain was found to be very uniform in structure, the pore diameters being approximately 0.2 micron (*i. e.*, in the area exposed, 1.54 sq. cm., 100 to 125 pores had diameters greater than 0.2 micron).[1] The thickness of the membranes was approximately 5 mm.

The cells used in the osmotic tests were of the simple form shown in Fig. 1. *A*, is a glass cylinder 15 mm. internal diameter with a capacity of about 6.5 cc. The procelain membrane *B* is held in place by a tight fitting rubber band which is in turn held firmly to the cell and to the membrane with copper wire. The outlet tube for measuring the osmotic effect is a capillary of 2 mm. internal diameter. The cell was supported about 15 mm. from the bottom of the beaker (800 cc.) by a tripod of heavy copper wire. A mark, *C*, was made on the capillary tube 50 mm. above the rubber stopper. At the beginning of an experiment the cell was filled to the mark on the capillary tube and the tripod was so adjusted that the surface of the liquid in the beaker was on a level with the liquid in the tube. Rise of liquids in the tubes, due to capillarity, was in no case greater than 8 mm. No corrections were made for capillary ascension in any of the following experiments, consequently, rise of liquids in the tubes to heights of 8 mm. or less cannot be interpreted as indicating osmotic effects: The heights of the liquids in the capillaries were read with a millimeter scale and estimated to 0 5 mm. The temperature, while not constant, was held at approximately 20°. Slight changes in temperature were not taken into consideration, inasmuch as all the experiments in each set were run simultaneously and comparative values only were desired. The volume of the liquid in the beakers in all the experiments was 750 cc. Loss of liquid from the beakers by evaporation was reduced to a minimum by the use of tightly fitting cardboard covers. Before starting the osmotic experiments, distilled water was drawn through the membranes by means of suction for at least 12 hours. No attempt was made to obtain maximum or quantitative effects, qualitative and comparable values only being sought. The results so obtained, however, have brought out some rather unexpected relations which seem sufficiently promising to warrant a further and more exacting research of a truly quantitative nature along similar lines.

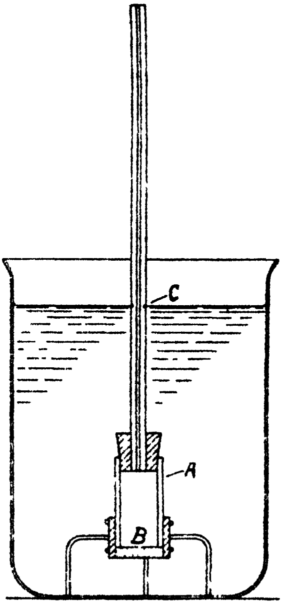

Fig. 1.

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[1] *Loc. cit.*

Experimental.

Cells constructed as above described were filled with sugar solutions of concentrations M,[1] M/5, M/20 and M/50. These cells were then placed in distilled water and tested. Positive osmotic effects were obtained with each of the solutions, the magnitude of the effects varying with the concentration. In the subsequent experiments the same grade of porcelain was used with solutions of sulfates, chlorides and nitrates of K, NH_4, Na, Li, Zn, Mn and Mg; also with acetates of K, NH_4, Na, Zn and Mn.

The salt solutions were put into the osmotic cells which were then placed in the beakers containing distilled water. The results, which are given in Tables I, II, III, IV, V, VI and VII, are expressed in millimeters and represent rise (+) or fall (—) from the zero mark (mark *C*) on the capillary tube:

TABLE I.

Concentration M/10. Chlorides (solution in cell).

	KCl.	NH_4Cl.	NaCl.	LiCl.[2]	$ZnCl_2$.	$MnCl_2$.	$MgCl_2$.
Apr. 11, 9 P.M.	0	0	0	0	0	0	0
Apr. 12, 9 P.M.	6	4	—4	— 9	—19	—17	—15
Apr. 13, 9 P.M.	12	6	—8	—18	—29	—29	—29
Apr. 14, 9 P.M.	20	12	—8	—24	—33	—35	—37.5
Apr. 15, 9 P.M.	25	15.5	—8	—27	—36.5	—39.5	—43
Apr. 16, 9 P.M.	27	17	—7.5	—29	—38.5	—43	—48
Apr. 17, 9 P.M.	28.5	19.5	—7	—31	—40.5	—46	—51
Apr. 18, 9 P.M.	28.5	20	—7	—32	—41.5	—47.5	.
Apr. 19, 9 P.M.	28	21	—7	—35	—44.5	—50	..
Apr. 20, 9 P.M.	27.5	21	—7	—34	—45	..	..
Apr. 23, 9 P.M.	26	21	—7	—34	—45	..	..

TABLE II.

Concentration M/10. Nitrates (solution in cell).

	KNO_3.	NH_4NO_3.	$NaNO_3$.	$LiNO_3$.	$Zn(NO_3)_2$.	$Mn(NO_3)_2$.	$Mg(NO_3)_2$.
Apr. 11, 9 P.M.	0	0	0	0	0	0	0
Apr. 12, 9 P.M.	11	5	—2	—18	—11	—15	—15.5
Apr. 13, 9 P.M.	21	11.5	—6.5	—33	—19	—26	—23
Apr. 14, 9 P.M.	32.5	19.5	—8	—44	—26	—32	—29
Apr. 15, 9 P.M.	39.5	26	—8	—50	—31	—37	—33
Apr. 16, 9 P.M.	43	29.5	—6	..	—34	—40	—36
Apr. 17, 9 P.M.	45	32	—5	..	—39	—44	—39
Apr. 18, 9 P.M.	47	33.5	—5	..	—42	—45	—41
Apr. 19, 9 P.M.	45	33.5	—5	..	—45	—49	—45
Apr. 20, 9 P.M.	45	33.5	—5	..	—47.5	—50	—46
Apr. 23, 9 P.M.	45	33	—5	..	—50	..	—48

[1] M, is used to indicate molecular normal.

[2] Other sets of experiments with these chloride solutions have since been carried out in a similar manner. In all the subsequent experiments LiCl was found to give greater negative effects (*i. e.*, greater negative osmose) than $ZnCl_2$, $MnCl_2$ or $MgCl_2$. The exceptional order of LiCl in this set of experiments is due to some cause unknown to the author. The original values are given in the tables in order to preserve the data of the entire series of experiments which were carried out simultaneously.

TABLE III.

Concentration M/10. Sulfates (solution in cell).

	K_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	Li_2SO_4.	$ZnSO_4$.	$MnSO_4$.	$MgSO_4$.
Apr. 11, 9 P.M.	0	0	0	0	0	0	0
Apr. 12, 9 P.M.	41	37	27	16.5	0	2	4
Apr. 13, 9 P.M.	67.5	57	42.5	27	—3	—2	2
Apr. 14, 9 P.M.	89	72	55	37.5	—4	—2	1
Apr. 15, 9 P.M.	99.5	80	61	43	—6	—4.5	—1
Apr. 16, 9 P.M.	103	82	62	46	—7	—6	—2
Apr. 17, 9 P.M.	105	84	62	46.5	—8	—9	—4
Apr. 18, 9 P.M.	103	83	60	46	—8	—9	—5
Apr. 19, 9 P.M.	98	80	58	44	—8	—9	—5
Apr. 20, 9 P.M.	96	80	57	43.5	—8	—9	—5

TABLE IV.

Concentration M/5. Sulfates (solution in cell).

	K_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	Li_2SO_4.	$ZnSO_4$.	$MnSO_4$.	$MgSO_4$.
May 17, 9 P.M.	0	0	0	0	0	0	0
May 18, 9 P.M.	54	43	29	3	—12	— 9	— 7.5
May 19, 9 P.M.	80	62.5	43	3	—16	—13	—11
May 20, 9 P.M.	89	72	49	1	—20	—16	—14
May 21, 9 P.M.	92	75	51	0	—22	—18	—16
May 22, 9 P.M.	91	75	51	0	—24	—19	—17

TABLE V.

Concentration M/2. Sulfates (solution in cell).

	K_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	Li_2SO_4.	$ZnSO_4$.	$MnSO_4$.	$MgSO_4$.
May 24, 9 P.M.	0	0	0	0	0	0	0
May 25, 9 P.M.	47.5	41	23	4	—12.5	—10.5	— 7
May 26, 9 P.M.	61	51	30	3	—15	—12	—13
May 27, 9 P.M.	81.5	68	40	0	—21	—16	—19
May 28, 9 P.M.	82	69.5	40	0	—23	—18	—21
May 29, 9 P.M.	81	69.5	39	0	—28	—24	—25

TABLE VI.

Concentration M/10. Acetates (solution in cell).

	$KC_2H_3O_2$.	$(NH_4)C_2H_3O_2$.	$NaC_2H_3O_2$.	$Zn(C_2H_3O_2)_2$.	$Mn(C_2H_3O_2)_2$.
May 31, 9 P.M.	0	0	0	0	0
June 1, 9 P.M.	73	48	39	—13	—10
June 2, 9 P.M.	99	53	51	—18	—14
June 3, 9 P.M.	115	55	60	—20	—15
June 4, 9 P.M.	121	55	64	—22	—16
June 5, 9 P.M.	122	55	64.5	—23	—17
June 6, 9 P.M.	123.5	55	65	—24.5	—18
June 7, 9 P.M.	123	54	65	—26	—20
June 8, 9 P.M.	123	53	64.5	—28	—21
June 9, 9 P.M.	121.5	51	64	—28.5	—21

It is noted that all the potassium and ammonium salts investigated gave positive osmose, sodium sulfate and sodium acetate gave positive osmose, lithium sulfate was also positive. All the other salts investigated gave negative osmose. The magnitudes of the negative effects are obviously greater than can be accounted for by differences in density or differences in surface tension of the solutions, in these instances, then the so-called exosmotic current is greater than the endosmotic current. The lowering of the liquid column is of considerable magnitude and must indicate a negative pressure within the cell. In order to obtain better data relative to the direction of flow, pure water was placed within the cells and the salt solutions (750 cc.) outside. The results obtained with this arrangement are as follows:

TABLE VII.

Concentration M/10. Chlorides (solution outside).

	KCl.	NH_4Cl.	NaCl.	LiCl.	$ZnCl_2$.	$MnCl_2$.
May 17, 9 P.M.	0	0	0	0	0	0
May 18, 9 P.M.	1	0	16	20	20.5	20.5
May 19, 9 P.M.	4	2	21	31.5	23.5	24.5
May 20, 9 P.M.	5	4	24	37.5	23.5	25
May 21, 9 P.M.	5	4	24	40	23	24.5
May 22, 9 P.M.	5	3.5	24	41	22.5	24
May 23, 9 P.M.	5	3.5	24	41	20	22.5

TABLE VIII.

Concentration M/5. Chlorides (solution outside).

	KCl.	NH_4Cl.	NaCl.	LiCl.	$ZnCl_2$.	$MnCl_2$.
May 24, 9 P.M.	0	0	0	0	0	0
May 25, 9 P.M.	5	1	20	29	15	15.5
May 26, 9 P.M.	9.5	5.5	25.5	43	18.5	19
May 27, 9 P.M.	12	8	28	52	20.5	20.5
May 28, 9 P.M.	12.5	7.5	28	53.5	20	20
May 29, 9 P.M.	12.5	7.5	28	53.5	20	19

TABLE IX.

Concentration M/10. Nitrates (solution outside).

	KNO_3.	NH_4NO_3.	$NaNO_3$.	$LiNO_3$.	$Zn(NO_3)_2$.	$Mn(NO_3)_2$.	$Mg(NO_3)_2$.
May 7, 9 P.M.	0	0	0	0	0	0	0
May 8, 9 P.M.	—3	—3	11	21	9	12	12
May 9, 9 P.M.	0	0	16.5	36	15.5	17	19
May 10, 9 P.M.	1	1	19	44	18	18	21
May 11, 9 P.M.	1	1	19	46	18	18	21
May 12, 9 P.M.	1	1	19	47	18	17	20
May 13, 9 P.M.	1.5	1.5	19	48	18	17	20
May 14, 9 P.M.	1	1	17	46.5	17	15	18
May 15, 9 P.M.	0	1	16	45	16	13	16

TABLE X.

Concentration M/5. Nitrates (solution outside).

	KNO_3.	NH_4NO_3.	$NaNO_3$.	$LiNO_3$.	$Zn(NO_3)_2$.	$Mn(NO_3)_2$.	$Mg(NO_3)_2$.
May 17, 9 P.M.	0	0	0	0	0	0	0
May 18, 9 P.M.	0	1	17	33	9	7.5	10
May 19, 9 P.M.	2	3	23	46	12	8	12
May 20, 9 P.M.	3	4	25	52	13	7	12
May 21, 9 P.M.	4	4	25	55	13	6	12
May 22, 9 P.M.	3	3.5	24.5	55	13	6	11.5
May 24, 9 P.M.	3	3	22.5	53	12	5	9

TABLE XI.

Concentration M/2. Sulfates (solution outside).

	K_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	Li_2SO_4.	$ZnSO_4$.	$MnSO_4$.	$MgSO_4$.
May 29, 9 P.M.	0	0	0	0	0	0	0
May 30, 9 P.M.	−2	−1	0.5	4.5	5.5	4.5	4.5
May 31, 9 P.M.	−4	−2	0.5	6	8	8	8
June 1, 9 P.M.	−3.5	−2	0.5	5.5	8.5	10	9
June 2, 9 P.M.	−4.5	−3.5	0.5	5.5	9	11	10
June 3, 9 P.M.	−5	−5	0.5	5	10	12	10.5
June 4, 9 P.M.	−5	−5	0.5	5	10	12	10
June 5, 9 P.M.	−5	−5	0.5	5	9.5	13	10

TABLE XII.

Concentration M/10. Acetates (solution outside)

	$KC_2H_3O_2$.	$NH_4C_2H_3O_2$.	$NaC_2H_3O_2$.	$Zn(C_2H_3O_2)_2$.	$Mn(C_2H_3O_2)_2$.
Oct. 20, 9 P.M.	0	0	0	0	0
Oct. 21, 9 P.M.	−13.5	−9	−5	6	6
Oct. 22, 9 P.M.	−19.5	−12	−6	6.5	7
Oct. 23, 9 P.M.	−20	−13	−6	7	8
Oct. 24, 9 P.M.	−21	−14	−6	6.5	9
Oct. 25, 9 P.M.	−21	−15	−6	6	9.5
Oct. 26, 9 P.M.	−21	−15	−6	5.5	9.5
Oct. 27, 9 P.M.	−20	−15	−6	5	9

The conditions of the above experiments were such that, had perfect semipermeable membranes been used, positive osmose theoretically should have been obtained in every case. The magnitude of the effects, although of the same order, would not have been identical, inasmuch as the solutions were not isotonic (owing to dissociation). The membranes used in these experiments were not semipermeable in the true sense of the word, but permitted the solute to diffuse outward into the pure water. In some cases this *diffusion produced a negative osmotic current which was greater than the positive osmotic current* and resulted in a flow of liquid which increased the volume of the dilute solution. This flow continued even though opposed by hydrostatic pressure which was in some instances as great as 50 millimeters. It seems reasonable to suppose, however, that there is in all cases a tendency to produce positive osmotic effects but that this tendency is, in those instances in which we obtain negative osmose, exceeded by some force which more than counterbalances the positive osmotic tendency.

From the above data it appears that the magnitude of negative osmose is closely related to the migration velocities of the ions. When the cations of the nitrate or chloride solutions are arranged in the order of increasing negative osmose values, this order is found to be the reverse of the order of increasing migration velocity values of these cations. It may be stated then that the greatest negative osmose is obtained with those solutions (of nitrates and chlorides) in which we have the greatest difference between the migration velocities of cation and anion. The sulfate and acetate solutions seem to offer some exceptions to the above rule; consequently, factors other than ionic migration velocities must also be taken into consideration to account for the order of negative osmose of these solutions.

Diffusion of Salt through the Membranes.—Experiments were carried out to determine the extent of salt diffusion during the negative osmotic flow. Pure water was placed within the cells, chloride solutions outside. Equivalent quantities of chloride solutions were used and showed a maximum pressure at the end of six days. The amount of chloride which had diffused into the cells during this period was determined by titrating the contents of the cells with standard $AgNO_3$ solution (M/10). The results are given in Table XIII. Column 2 gives the number of cc. of M/10 $AgNO_3$ solution which was required to precipitate the chloride which had diffused into the cell during the experiment (six days). Column 3 gives the relative equivalent quantities of chlorides which had diffused into the cells (KCl = 1):

TABLE XIII.

	Cc. $AgNO_3$ required.	Equivalents of salt diffused.
M/5 KCl	3.50	1.000
M/5 NH_4Cl	3.00	0.857
M/5 NaCl	2.80	0.799
M/5 LiCl	2.15	0.614
M/10 $ZnCl_2$	2.60	0.743
M/10 $MnCl_2$	2 50	0.714

This experiment brought out the interesting fact that the cells which have the greatest flow of liquid, as a whole, into them (when set up in this reverse order) have, on the other hand, the smallest quantities of the salts diffusing into them.

Nernst[1] pointed out that the diffusion velocity of salts is proportional to the product of the velocities of the cation and anion. J. C. Graham[2] has shown experimentally that this generalization holds for a large number of salts investigated by him and also that, when the cations and anions are arranged according to diffusion velocities, the order is very similar to that when they are arranged according to their mobilities under influence of electric potential. That this order is also similar to the order of diffusion quantities of the corresponidng salts through porcelain membranes is shown by the following table. Column 1 gives values representating relative diffusion velocities of the salts (Graham). Column 2 gives the relative ionic migration velocities of the cations (Arrhenius). Column 3 gives the ratio of equivalent quantities of salts which diffused through the porcelain membranes:

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[1] *Z. physik. Chem.*, 2, 613 (1888).

[2] *Ibid.*, 59, 691 (1907).

TABLE XIV.

Salt.	1.	2.	3.
KCl	1.000	1.000	1.000
NH_4Cl	0.984	0.983	0.857
NaCl	0.744	0.673	0.799
LiCl	0.718	0.517	0.641
$ZnCl_2$	0.558	0.722	0.743
$MnCl_2$	0.584	. .	0.714

Dutrochet[1] was the first to give an account of negative osmose with inorganic membranes (1827).

Thomas Graham[2] observed a negative osmotic flow in connection with his work with solutions of electrolytes and porcelain membranes. He did not, however, measure either positive or negative pressures; in fact, he prevented inequality of pressure on the membrane by keeping the level of the water adjusted to the height of the liquid in the "osmometer" tube and measured only the change in volume of the solution. The apparent irregularities obtained with porcelain membranes and solutions of electrolytes were believed by him to be due mainly to chemical interaction between electrolyte and membrane. Solutions of alkalies gave negative effects and it was believed that "The caustic alkalies have probably too strong a disorganizing action upon the septum to allow osmose to proceed undisturbed." Owing to the unsatisfactory behavior of the porous membranes he did not give results of his "numerous experiments which had been made with the earthen osmometer" but confined his data to work with other membranes which had proved less troublesome. In general, the results obtained by Graham with porcelain membranes are very similar to the results given in this paper. The irregularities encountered by him can be explained by use of the theory which is outlined in the theoretical part of this paper and which is offered to account for the behavior of solutions of electrolytes in the osmotic cells of porcelain above described.

Relation of Pore Diameter to Negative Osmose.—A number of experiments have been carried out to determine to what extent pore diameter effects negative osmose. With M/10 $MgCl_2$ solutions, and with porcelain membranes having pore diameters greater than 0.4 micron, no apparent osmotic effects were obtained. With pore diameters between 0.4 and 0.1 micron negative osmose was noted. By using a denser grade of porcelain, one with pore diameters somewhat less than 0.1 micron, positive osmose was obtained, *i. e.*, the flow was in the direction that is usual with osmotic experiments when "semipermeable" membranes are used. It seems probable, therefore, that negative osmose with $MgCl_2$ solution predominates only when pore diameters of the membrane lie between the 0.1 and 0.4 micron value. With pore diameters greater than 0.4 micron there is no measurable flow through the membrane. With pore diameters somewhat less than 0.1 micron positive osmose predominates.

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[1] *Ann. Chim.*, 35, 393 (1827).

[2] *Phil. Trans.*, 144, 177 (1854).

Theoretical.

A consideration of the above described experiments makes it seem probable that the phenomenon of negative osmose is closely related to the process of electric endosmose and that the flow of liquid through the membrane is brought about by a difference in electric potential, the two ends of the capillaries of the membrane becoming, in some way, oppositely charged.

Potential differences have been shown to exist in such membranes as animal cells,[1] frog muscle,[2] vegetable skins,[3] and other living tissue;[4] also membranes of copper ferrocyanide,[5] clay[6] and other insoluble substances. Nernst's theory of potentials in which use is made of the well known formula, $E = \frac{RT}{nF}\frac{U-V}{U+V}\ln\frac{C_1}{C_2}$,[7] together with the theory of selective permeability of the ions, has been employed in practically all such cases to account for this phenomenon.

While Nernst's theory may account for the difference in potential existing between two solutions of different concentrations it does not, alone, account for the polarization of the capillaries and flow of solution through the membrane. The polarization of such membranes has been ascribed by Perrin[8] to be due to contact electrification, the potential of the wall being largely dependent upon the preponderance of H ion or OH ion. Girard[9] found that this theory satisfactorily accounted for the direction of flow of various solutions in osmotic experiments with membranes of pig bladder. Unquestionably the relative absorption of the cations and anions by the membrane must also be taken into consideration in order to account for the polarization; however, it appears that this adsorption is closely related to ionic migration velocities.

Cohen[10] was led to the conclusion that a substance having a lower dielectric constant than the liquid in which it is placed assumes a negative charge. Porcelain placed in water would give the Helmholtz double layer,[1] the porcelain bearing the negative charge, the outer layer of water the positive charge. It has been shown by Perrin[2] that a porous membrane in sufficiently strong acid solution becomes charged positively, while in sufficiently strong alkaline solution the membrane becomes charged negatively. Electric endosmose with a porcelain membrane and a sufficiently strong acid solution produces, then, a flow of solution through the membrane from cathode to anode; with an alkaline solution the direction of flow is from anode to cathode.

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[1] Oker-Blom, *Pflüger's Archiv.*, 84, 191 (1901). Ostwald, *Z. physik. Chem.*, 6, 71 (1890).

[2] Brünings, *Pflüger's Archiv.*, 48, 241 (1903).

[3] Loeb and Beutner, *Science*, 34, 866.

[4] Lillie, *Am. J. Physiol.*, 28, 194 (1911). Girard, *Revue générale des Science*, 20, 694 (1909).

[5] Beutner, *J. Phys. Chem.*, 17, 344 (1913).

[6] Brünings, *Pflüger's Archiv.*, 117, 409 (1907).

[7] Nernst, *Z. physik. Chem.*, 9, 137 (1892).

[8] *J. chim. phys.*, 2, 601 (1904).

[9] *Loc. cit.*

[10] *Wied. Ann.*, 64, 217 (1898).

The sign of the charge on a membrane depends, undoubtedly, on the relative adsorption of cation and anion. The membrane becomes positive if the cation, and negative if the anion, is adsorbed to the greater extent.[3] By taking into consideration the relative adsorption of all ions present the polarization of the membrane and the direction of flow of the solution can thus be accounted for. If we assume, for instance, that adsorption of relatively more cation than anion were to take place at one end of a capillary, that end would become charged positively and would, therefore, function as does the anode in the process of electric osmose. The direction of flow through a tube so polarized would be toward the end charged negatively. In the various salt solutions the differences in potential would, to a large extent, depend on the relative adsorption of the ions by the walls of the tube and on the concentration of the solutions. To account for the relative osmose of the sulfates, chlorides and nitrates in the above experiments we must assume that relatively more sulfate ion is adsorbed than chloride or nitrate ion.[4] In a porcelain membrane we are undoubtedly dealing with a somewhat complex system of short capillaries;[5] however, the same reasoning can be applied.

The well known fact that the amount of a dissolved substance adsorbed by a solid mass increases much more slowly than the concentration of the solution would account for the comparatively slight differences of osmose with the different concentrations.

Summary.

1. Salt solutions of sulfates, chlorides, nitrates and acetates were placed in osmotic cells which were constructed of porcelain membranes of the same degree of porosity. Some of the solutions gave positive osmose, *i. e.*, the direction of flow of liquid was from the dilute to the more concen-

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[1] *Wied. Ann.*, 7, 351 (1879).

[2] *Loc. cit.*

[3] Bancroft, *J. Phys. Chem.*, 16, 312 (1912).

[4] These results are in accord with assumptions made by Bancroft in order to explain some apparent exceptions to the general rule in experiments of electric osmose. *Loc. cit.*

[5] Bigelow, THIS JOURNAL, 29, 1675 (1907).

trated solution; others gave negative osmose; the direction of flow in these unusual cases was from the concentrated to the more dilute solution.

2. Cells were set up with pure water inside and salt solutions outside. When set up in this reversed manner, the solutions which had previously given decreased pressure within the cells now gave increased pressure, that is, the direction of flow was from concentrated to dilute solution even though opposed by hydrostatic pressure.

3. The quantities of the salts which diffused through the membranes were determined. It was found that the order of diffusion quantities of the salts through the porcelain membranes is practically the same as the order of diffusion velocities when no membrane is present. Also it was found that the membranes which have the greatest negative osmose through them have, on the other hand, the smallest quantities of salts diffusing through them.

4. The flow of the solution as a whole through the membrane, in all the experiments with the nitrates and chlorides, was toward the more dilute solution, provided the anion had a somewhat greater migration velocity than the cation; also the greater the difference between the migration velocities of anion and cation the greater the rate of flow.

5. It has been shown that the appearance of negative osmose is dependent on the pore diameter of the membrane. Negative osmose of $MgCl_2$ in neutral solution, and with porcelain membranes, predominates only when the pore diameters are somewhat less than 0.4 micron.

6. The facts brought out in this investigation seem to indicate that negative osmose is dependent on the electrical polarization of the capillaries of the membrane, also it seems probable that this polarization is largely brought about through ionic adsorption by the membrane.

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NOTE.

Convenient Standard End Point in the Titration of Alkali Carbonates with Hydrochloric Acid.—As long ago as 1897, Küster[1] pointed out that, in the titration of sodium carbonate against hydrochloric acid, when equivalent amount of acids and base have been used, the solution contains free carbonic acid, and that this acid exerts an appreciable effect on the color of an aqueous solution of methyl orange. A tenth normal solution of carbonic acid, which results from titration with fifth normal solutions, is a little more than saturated with carbon dioxide at 20°.

Küster recommends adjusting the color of the solution obtained in titration to that of a saturated aqueous solution of carbon dioxide containing methyl orange. Unfortunately, this standard end point is not permanent, even in corked vessels, owing probably both to the escape of carbon dioxide and to the solubility of the alkaline constituents of the glass, and hence it must frequently be renewed. A similar color with methyl orange obviously may be produced by aqueous solutions of other acids or acid salts of suitable concentration. Of these, monopotassium and monosodium phosphate are particularly well adapted for the purpose, since the acidity of solutions of these substances is affected relatively slowly by the addition of acids or alkalies. Although the dissociation constant of the second hydrogen of phosphoric acid, 2×10^{-7}, is nearly identical with that of the first hydrogen of carbonic acid, 3×10^{-7}, the acidity of a solution of monosodium phosphate is somewhat less than that of an *equivalent* solution of carbonic acid, owing possibly to hydrolysis. Comparison of the color of a saturated aqueous solution of carbon dioxide, containing methyl orange, and solutions of monosodium phosphate of various concentrations, also containing methyl orange, shows that the carbonic acid solution is perceptibly less acid than a phosphate solution containing 20 g. of crystals[1] in 100 g. of water, more so than one containing 15 g. of crystals in 100 g. of water, while a solution of 17.5 g. of crystals in 100 g. of water possesses apparently the same color as the carbonic acid solution. An equivalent solution of monopotassium phosphate, containing 15.3 g. of crystals[2] was found to be identical in color with the solutions of the sodium salt. Since the hydrogen ion concentration of a carbonic acid solution changes only from about 2.5×10^{-4} to 1.2×10^{-4} between the limits of 0.2 normal and 0.05 normal, and since this difference in the hydrogen ion concentration corresponds to only 0.06 cc. fifth normal hydrochloric acid in 100 cc., and since, by escape of carbon dioxide, more concentrated solutions tend to approach a concentration of tenth normal, it is obvious that the above end point can safely be used in the titration of solutions from half to tenth normal.

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[1] *Z. anorg. Chem.*, 13, 141 (1897).

Before being used, both salts should be crystallized to free them from phosphoric acid or disodium phosphate. Owing to its lesser solubility, the potassium salt is somewhat more easily purified and therefore better adapted for the purpose.[3]

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OBSERVATIONS ON SOME BARBIER-GRIGNARD REACTIONS.

BY L. P. KYRIAKIDES.

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Methylethylethylene chlorhydrin: Chloro - 1 - methyl - 2 - butanol - 2, $CH_3.CH_2.C(CH_3)(OH).CH_2Cl$.—The chlorhydrins are usually obtained by the addition of hypochlorous acid to the unsaturated hydrocarbons.

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[1] $NaH_2PO.2H_2O$. This hydrate crystallizes between 41° and 0°. Imadsu, *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, 3, 257 (1912).

[2] KH_2PO_4.

[3] This was pointed out to me by Dr. H. H. Willard.

M. Tiffeneau[1] has prepared some of the unsymmetrical chlorhydrins by the action of organomagnesium compounds on chloroacetone. In a paper on these preparations, he observes that he obtained chloro-1-methyl-2-butanol-2, with a yield of 72%, by the action of ethylmagnesiumbromide on chloroacetone. In a later paper by Fourneau and Tiffeneau[2], we read that the substance, described in the latter's previous paper, with the boiling point 149–151°, was not a homogeneous compound. They discovered that the reaction product consisted of a mixture of two compounds, both boiling at identically the same temperature; so that they could not be separated by fractional distillation. One of these substances was the normal Barbier-Grignard reaction product, boiling at 152–153°. The by-product consisted of ethyl-2-pentanol-3, $CH_3.CH(CH_2.CH_3).CH(OH).CH_2.CH_3$, boiling at 150°. This latter substance must have been formed by the action of the organomagnesium compound on either methyl-2-butylene-oxide-1,2$(CH_3.CH_2.\overbrace{C(CH_3).CH_2}^{O})$ or its metamer, methylethylacetaldehyde $(CH_3.CH_2.CH(CH_3).CHO)$ either of which might have been formed from the chloroalcohol during the reaction. The authors separated the two compounds by transforming the chlorhydrin to the oxide, whose boiling point is much lower than that of the alcohols.

Having discovered that oxides could be easily dehydrated to the corresponding hydrocarbons with conjugated double bonds, we undertook the study of Tiffeneau's synthesis. We were soon confronted with the fact that the yields of oxide, obtained by the treatment of the crude Barbier-Grignard reaction product with potassium hydroxide, varied within wide limits. In fact, at times it seemed that the side products were the main result of the reaction. These variations were found to be due to thermochemical causes. As the heat evolved in the action of chloroacetone on ethylmagnesium bromide is very great, local heating plays a prominent part during the reaction.

The Barbier-Grignard reaction is therefore carried out as follows: 67 g. magnesium turnings are put in a $2^1/_2$ liter bottle provided with a condenser and then covered with 750 cc. dry ether. The Grignard reagent is prepared by gradually adding a solution of 307 g. ethylbromide in 300 cc. dry ether. The reagent is treated with 400 cc. more ether, cooled by means of ice and salt to below —10°, and treated slowly, at such a rate that the drops can be counted, with a solution of 250 g. chloroacetone in 250 cc. ether. The bottle is kept in vigorous motion during the addition, which takes about $1^1/_2$ hours. The freezing mixture is renewed several times, in order to keep the temperature of the reaction mixture as low as possible. In this way, the addition product is obtained in pulverulent form, floating throughout the liquid. The vigorous shaking, besides, hinders the addition product from falling into lumps and enclosing any of the free Grignard reagent. The reaction product prepared in this way is almost colorless, having at most only a very light yellow tinge. After the addition of the chloroacetone, the condenser is taken off, the bottle is stoppered, the latter shaken for a short time, and left in ice for an hour or two. The decomposition of the products is effected with ice and dilute acetic acid. The ethereal solution is washed several times with water, shaken with powdered calcium carbonate, dried over calcium chloride, and the ether distilled off through a column, until the water bath attains a temperature of 90–95°.

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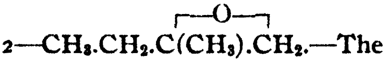
[1] *Compt. rend.*, 134, 774 (1902).

[2] *Ibid.*, 145, 437 (1907)



Methyl-2-butyleneoxide-1,2—$CH_3.CH_2.C(CH_3).CH_2$.—The residue obtained above, after distilling off the ether, is cooled with ice-water and treated slowly, while shaking, with a cold solution of 220 g. potassium hydroxide in 150 cc. water. After a short shaking, the upper layer is separated, dried over potassium carbonate, and the oxide is obtained by fractional distillation through a column. The aqueous alkaline layer is shaken once with a little ether, the ethereal layer dried, and fractioned separately. The crude oxide fractions are united and refractioned. The fraction boiling 78-85° is collected as oxide. This fraction, boiling mostly at 80–83°, weighed over 150 g., and contained traces of the metameric methylethylacetaldehyde. The yield of oxide was, therefore, over 65% of the theoretical on the magnesium originally used.[1] As the oxide is easily hydrolyzed, it is possible that some of it may have been transformed to the corresponding glycol, which might have been present in the residues from the oxide. These residues were not studied, further than that some small amounts of Fourneau and Tiffeneau's compound—ethyl-2-pentanol-3—could be isolated.

It is the belief of the writer that, by more efficient cooling and shaking of the Grignard reagent during the addition of the chloroacetone, the yield of methylchlorobutanol, and consequently that of the oxide, can be further increased.

Barbier-Grignard Reactions with Ethylchloride.—As far as I know, ethylchloride has not been hitherto used in ordinary organomagnesium reactions. Spencer and Mary Crewdon[2] describe the action of magnesium on ethylchloride at 260°, whereby they obtain a mixture of gases, consisting of butane, olefines and hydrogen.

As the use of ethylchloride instead of the bromide would be more advantageous on the large scale, I have thought of making use of it in preparing the Grignard reagent. The results obtained were excellent. The reagent was prepared as follows: 77 g. magnesium, in a 2-liter thick-walled bottle, were covered with 1 liter dry ether, and treated with a crystal of iodine and 1 cc. methyl iodide. The bottle was then cooled in ice-water and 34 g. ethylchloride were condensed in the ether. The bottle was closed tightly with a rubber stopper carrying a thermometer, whose bulb dipped within the ether, and the latter was warmed at its boiling point for some time. The liquid was then cooled down and about 60 g. ethyl chloride were condensed in it. The solution was then warmed again, and the process repeated until in all about 220 g. of the chloride had been added. This amount of the chloride is a little more than the theoretical amount required by the magnesium used. The metal is very smoothly and rapidly attacked, once the reaction is made to begin. In this preparation about 5 g. of the metal were left unattacked. It is to be observed that, as this reaction was carried out in a closed vessel, there would be no appreciable loss of ether or ethylchloride.

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[1] As in the preparation of the Grignard reagent, 5 g of magnesium had not gone in solution, the yield of oxide would be 68%.

[2] *Chem Zentr*, **1909**, I, 146.

The Grignard reagent was cooled and treated with a solution of 275 g. chloroacetone—equivalent to 72 g. magnesium—in an equal volume of ether. In spite of the fact that this addition was not carried out very carefully, I obtained 153 g. of methylethylethyleneoxide from the crude reaction product. This amount of the oxide corresponds to about 60% of the theoretical yield on the chloroacetone used.

A similar reaction between ethylmagnesium chloride and acetone gave over 70% of tertiary amylalcohol—$(CH_3)_2C(OH).CH_2.CH_3$.

One of the advantages of using ethylmagnesiumchloride in the preparation of methyl-2-butylene oxide-1,2, is the fact that the addition product with chloroacetone is much more soluble in ether than the ethylbromide product. With the proportions of substances used in the example above, there is no separation of any solid products. In this case, therefore, the liquids can be cooled much more easily and local heating can be better avoided.

It has been our experience that Barbier-Grignard reactions give normal results, as a rule, when the addition of the substances containing the carbonyl group to the Grignard reagent is carried out slowly, with constant shaking and very efficient cooling. This has already been noted in the case of chloroacetone, where, because of the mobility of the chlorine atom, there is a marked tendency for abnormal reactions.

Kohler[1], having carried out a great number of organometallic reactions with unsaturated ketones, observes that the Grignard reagent has a marked tendency to add itself at the double bond. In these cases he obtained, besides the normal reaction products—the unsaturated tertiary alcohols—

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[1] *Am. Chem. J.*, 38, 511 (1907).

also varying quantities of the saturated ketones. These two products are the results of two reactions taking place simultaneously, namely:

I. $R.CH : CH.CO.R + R_1 MgX =$

$$R.CH : CH.C(RR_1).OMgX \longrightarrow R.CH : CH.C(RR_1)(OH).$$

II. $R.CH : CHCOR + R_1MgX =$

$$(RR_1)CH.CH : CROMgX \longrightarrow (RR_1)CH.CH_2.COR.$$

R may stand for an alkyl or an aryl residue.

Kohler, on the basis of the results he obtained, concluded that the relative amounts of the final products in these organometallic reactions depend upon "the nature of the unsaturated compound, the number and arrangement of the hydrocarbon residues, the character of the magnesium derivative, and *possibly, temperature, concentration*[1] and solvent."*

In his experiment with ethylidene acetone and methylmagnesium bromide, Kohler, having used two molecules of the magnesium compound to one of the ketone, obtained a product which consisted 75% of methylisobutylketone and only 25%, at most, of the normal reaction product—methyl-2-penten-3-ol-2. He isolated and determined the ketone after oxidizing the unsaturated alcohol with dilute permanganate solution.

Gry[2], on the other hand, observes that the interaction of equimolecular quantities of methylmagnesiumiodide and ethylidene acetone resulted in the formation of considerable quantities of the unsaturated tertiary alcohol —$CH_3.CH : CH.C(CH_3)_2(OH)$. He also states that, although he obtained products with high boiling point, he "did not encounter any ketonic products." Comparing the statements and the results of the above quoted authors, one would assume that the difference in results lay in the relative amounts of the Grignard reagents used in each case.

As unsaturated alcohols—especially those with a tertiary hydroxyl group—are easily dehydrated to doubly unsaturated hydrocarbons, we undertook the preparation of methyl-2-penten-3-ol-2 by means of the Barbier-Grignard reaction.

The reagent (1 1/2 mol) was prepared as usual from magnesium and methyliodide in dry ether. It was then cooled by a freezing mixture to below —10°. The ethereal solution of ethylidene acetone (1 mol) was added slowly to the reagent, while the latter was kept in vigorous motion. The reaction mixture was left at room temperature for a short time, and then decomposed with ice and dilute acetic acid. The ethereal solution and the extracts were shaken with dilute sodium hydroxide solution, dried over potassium carbonate, and the ether distilled off through a column. The residue was fractioned *in vacuo*. We obtained in this way over 80% of the theoretical yield (on the ketone used) of a liquid that boiled at about

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[1] The italics are mine.

[2] *Bull. soc. chim.*, [4] 3, 377 (1908).

80° at 145 mm. The residues from this liquid showed signs of dehydration, and were not studied any further.

In order to determine the nature of the distilled product, we made use of a method of mine, which I shall describe in a later paper, whereby the tertiary alcohol could be quantitatively dehydrated to the corresponding diethylenic hydrocarbon.

On dehydrating the liquid, the dehydration products were found to consist to the extent of 75% of a doubly unsaturated hydrocarbon, whose constitution is very probably $CH_3.CH : CH.C(CH_3) : CH_2$. and not $CH_3CH : C : C(CH_3)_2$ as given by Gry.[1] This hydrocarbon boils at 76–77°—Gry gives its boiling point as 76–79°. The residues from the hydrocarbon consisted mostly of the tertiary alcohol itself, which was carried over by the water of dehydration during the distillation of the reaction products. This was proven to be the case by treating the above residues in the same way as the original liquid. By repeating this dehydration process we were able to transform practically all of the Barbier-Grignard reaction product to the hydrocarbon. From a total of 40 g. unsaturated alcohol used, we could obtain barely 1 g. of a liquid, which could be identified as methylisobutylketone.

The reaction, therefore, seems to have proceeded normally:

$$CH_3.CH : CH.COCH_3 + CH_3MgI = CH_3CH : CHC(CH_3)_2OMgI \longrightarrow CH_3CH : CHC(CH_3)_2(OH).$$

From the above results it would seem that the concentration of the Grignard reagent does not have any appreciable effect on the course of the reaction. If it were otherwise, both Gry and I ought to have had considerable amounts of methylisobutylketone. The reaction in all three cases was carried out by the gradual addition of the ketone to the ethereal solution of the organometallic compound. In every case, therefore, the magnesium compound was in great excess at the beginning of the reaction.

Hence, if concentration played any important part, the final results in all three cases ought to have been of the same nature. In the experiment described above, I had $^1/_2$ mol of the Grignard reagent in excess, and yet the result was not anywhere comparable with that obtained by Kohler. There can be no doubt, as Kohler asserts, that the course of the Barbier-Grignard reaction is influenced by the character of the reacting components. There must be other conditions, however, which influence the reaction very markedly.

I am of the opinion that efficient cooling,[2] and vigorous shaking during the reaction—at least in the case discussed here—exert a normal influence, whereby the unsaturated alcohol is obtained as the main product.

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[1] *Bull. soc. chim.*, [4] 3, 377.

[2] These observations agree with those of Latham Clarke in the reaction between saturated ketones of fairly high molecular weight and organomagnesium compounds [This Journal, 34, 680 (1912)].

I might also mention here, that by following these conditions, we were able to improve the yields in unsaturated secondary alcohols from crotonaldehyde and alkylmagnesiumhalides.

Thus we have obtained 90% of the theoretical yields of penten-2-ol-4 and hexen-2-ol-4 from the aldehyde and methylmagnesiumiodide and ethylmagnesiumbromide, respectively.

Hydrolysis of Methyl-2-butyleneoxide-1,2.—10 g. oxide were boiled with 20 cc. water in a flask provided with a reverse cooler. The oxide layer began to decrease immediately and within 5 minutes disappeared completely. The oxide was, therefore, totally hydrated to the glycol, excepting for a minute quantity of methylethylacetaldehyde, which might have been present originally in the oxide.

Another sample of the oxide was left in contact with water at room temperature. The oxide layer had decreased in volume by only $^1/_3$ in 12 hours. Shaking would, naturally, increase the rate of hydration.

Conclusions.

Barbier-Grignard reactions with aliphatic ketones and aldehydes give better results if carried at low temperatures. Vigorous shaking is necessary to avoid local heating. This precaution is of absolute necessity in the case of substances containing mobile halogen atoms.

Organomagnesium reactions can be effected with the use of ethylchloride. The use of this substance is of especial advantage in the preparation of chloro-1-methyl-2-butanol-2, as the addition product between the alkylmagnesiumchloride and chloroacetone is quite soluble in ether.

In conclusion, I wish to express my thanks to R. B. Earle, for assisting me in these investigations.

CAMBRIDGE, MASS.

NEW PROCESSES FOR THE PREPARATION OF UNSATURATED HYDROCARBONS WITH CONJUGATED DOUBLE BONDS.

[FIRST PAPER.]

BY L. P. KYRIAKIDES

Received February 2, 1914

Pyrogenetic Decomposition of Oxides.

The most important representative of the butadiene-1,3 hydrocarbons is isoprene. This substance can be transformed to a rubber-like body, and is supposed to be the mother-substance of the natural product. Isoprene seems to have been first isolated by G. Williams, who also observes that "ozonized isoprene," on distilling off the more volatile portion, gradually becomes thicker, and finally, "the contents of the retort in-

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[1] *J. Chem. Soc.*, 15, 110 (1862).

stantly solidify to a pure white, spongy, elastic mass, having, when successfully prepared, but slight tendency to adhere to the fingers." Later, Bouchardat,[1] having treated isoprene in the cold with 12–15 parts of hydrochloric acid, saturated at 0°, and shaken the mixture occasionally in a sealed tube at ordinary temperatures during 15–20 days, isolated considerable quantities of a solid residue. This product was found to "possess the percentage composition of isoprene....and the elasticity and other characteristics of caoutchouc itself..... All of these properties seem to identify this polymer of isoprene with caoutchouc—the product from which isoprene is generated." Tilden[2] remarks that isoprene, obtained by the pyrogenetic decomposition of turpentine, formed rubber. The latter, he observes "appears to be produced most readily from the oily polymeride, resulting from the action of heat. Contact with strong acids in the cold effects the change."

The remarks of the above quoted authors led later investigators to study the conditions for the polymerization of isoprene to rubber. As a rule, however, their attempts failed to give any positive results. It was not until Fritz Hofmann of the Elberfelder Farbenfabriken, and Harries soon afterwards, succeeded in polymerizing isoprene to rubber, that polymerization was definitely established. Hofmann[3] and Harries[4] also observed that even the homologues of isoprene could be changed to rubber-like masses by the same process. Since the discovery of the last named investigators, a great amount of work has been carried out with a view to the synthetic production of the butadiene-1,3-hydrocarbons. The number of patents that have been issued in the last few years on the synthesis of these hydrocarbons is strong testimony to the importance of the technical production of rubber. The writer does not intend to enter into any discussion as regards the relative merits of these patents, either from a scientific or technical point of view. A good many of the patents, in my estimation, have no practical value at all; while others, being merely the result of theoretical reasoning, could not be carried out in practice.

Isoprene, $CH_2 : C(CH_3).CH:CH_2$.—α-Oxides, when passed through glass tubes heated at 500°, undergo a metamerization, giving rise to aldehydes or ketones, or both, depending on the molecular structure of the oxides. Ipatieff and Leontovitch,[5] who first studied these pyrogenetic reactions, observed also that heated catalysts, such as aluminum oxide, effect the metamerization of the α-oxides at a much lower temperature. These investigators obtained a mixture of methylisopropylketone and methyl-1-butyraldehyde, by passing trimethylethyleneoxide, which contained some of the isomeric substance, methyl-2-butyleneoxide-1,2 over aluminum oxide at 250–260°. These reactions took place as follows:

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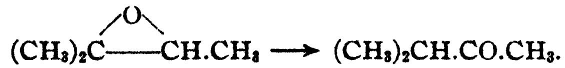
[1] *Compt. rend.*, 89, 1118 (1879).

[2] *J. Chem. Soc.*, 45, 415 (1884).

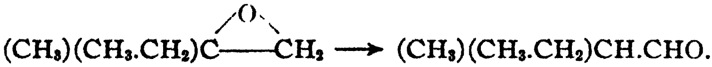
[3] *Chem. Zentr.*, 1911, II, 175, 176.

[4] *Ann.*, 383, 190, 210 (1911).

[5] *Ber.*, 36, 2016 (1903).

(1) 

$$(CH_3)_2C\overset{O}{\text{——}}CH.CH_3 \longrightarrow (CH_3)_2CH.CO.CH_3.$$

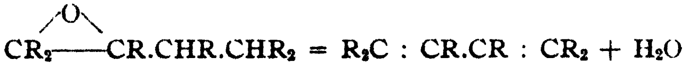
(2) 

$$(CH_3)(CH_3.CH_2)C\overset{O}{\text{——}}CH_2 \longrightarrow (CH_3)(CH_3.CH_2)CH.CHO.$$

Ipatieff and Leontovitch have also observed that amylene oxide, passed through a glass tube heated at 600°, suffered partial decomposition. At this temperature (in absence of aluminum oxide) they obtained, besides the ketone and aldehyde, a mixture of gases consisting of saturated and unsaturated hydrocarbons, hydrogen, carbon monoxide and dioxide. This metamerization of oxides to ketones or aldehydes is also readily effected at much lower temperatures by substances having an acid reaction.

One of the best known methods for preparing olefins is by the dehydration of saturated alcohols by substances known generally as dehydrating catalysts, such as the oxide, silicate of aluminum, etc. These reactions have been studied by Ipatieff, Sabatier, Senderens and others.[1]

In June of 1911, I discovered that oxides can be dehydrated to the corresponding diolefines with conjugated bonds, according to the following scheme:



$$CR_2\overset{O}{\text{——}}CR.CHR.CHR_2 = R_2C : CR.CR : CR_2 + H_2O$$

where R may be a hydrogen atom or an organic radical. It will be seen that this dehydration is similar to that of the saturated alcohols, as in both cases one molecule of water is split off from each molecule of the substance brought into reaction.

The methyl-2-butyleneoxide-1,2 used in the following experiments was prepared from chloro-1-methyl-2-butanol-2. The latter substance was obtained, as described in the previous paper, by the action of methylmagnesiumhalide on chloroacetone:

Experiment 1.—Fifty grams of the oxide were passed through a glass tube heated at about 400° and containing a layer of aluminum silicate in the form of fine powder. The length of the silicate layer was about 50 cm. The oxide was introduced into the tube in drops, and the distilling substance collected in a receiver cooled with ice and salt. The distillate was separated from the water, dried over calcium chloride, and fractioned through a column. Eleven grams of the liquid distilled over between 30–45°, and 20 g. distilled over at 80–95°, mostly about 90°.

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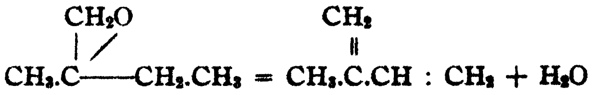
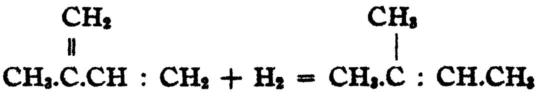
[1] *Lehrbuch der Org. Chemie*, Meyer and Jacobson, Second ed., 1, I, 817–818.

This latter substance consisted of impure methyl-1-butanal, formed by the metamerization of the oxide, as previously observed by Ipatieff and Leontovitch. The liquid boiling at 30–45° was refractioned, and the portion boiling between 30–40° (mostly 33–38°) was dissolved in ether, cooled in ice, and treated gradually with bromine. The brominated compound was found to consist of approximately equal amounts of trimethylethylene and isoprene dibromides.[1] Trimethylethylene could not have been formed normally from the oxide, as the dehydration product could be only a hydrocarbon containing two double bonds. And as will be seen later, isoprene being the normal dehydration product of the oxide, trimethylethylene could have been only formed by the secondary reduction of the isoprene.

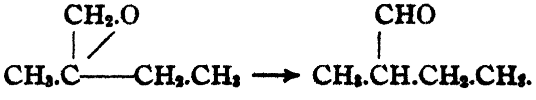
Now, it is found that during the pyrogenetic catalysis of the oxide, the catalyst is soon covered with a layer of carbon, so that its activity steadily decreases and eventually stops altogether. The result of this is, that, as carbonization progresses, the relative amounts of methylethylacetaldehyde(methyl-1-butanal) distilling over increase, and towards the end the only result of the distillation of the oxide over the catalyst is a simple metamerization of it to the aldehyde. Carbonization is also evidence of a more or less general decomposition of the carbon chain, resulting in the formation of gaseous products. These may be similar in nature to those observed by Ipatieff and Leontovitch in the case of the mixture of amylene oxides. Hydrogen being one of these decomposition products, it stands to reason that isoprene is reduced by it to trimethylethylene. The three main reactions in the dehydration of methylbutylene oxide may be represented as follows:

(1) 

$$CH_3.\overset{\overset{\displaystyle CH_2O}{|\;/}}{C}\!\!-\!\!-\!\!CH_2.CH_3 = CH_3.\overset{\overset{\displaystyle CH_2}{\|}}{C}.CH : CH_2 + H_2O$$

(2) 

$$CH_3.\overset{\overset{\displaystyle CH_2}{\|}}{C}.CH : CH_2 + H_2 = CH_3.\overset{\overset{\displaystyle CH_3}{|}}{C} : CH.CH_3$$

(3) 

$$CH_3.\overset{\overset{\displaystyle CH_2.O}{|\;/}}{C}\!\!-\!\!-\!\!CH_2.CH_3 \longrightarrow CH_3.\overset{\overset{\displaystyle CHO}{|}}{CH}.CH_2.CH_3.$$

Commenting on the pyrogenetic decomposition of turpentine to isoprene, Harries and Gottlob[2] observe that they obtained varying yields of the hydrocarbon, depending on the dipentene contained in the commercial product. Staudinger and Klever,[3] on the other hand, observe that by decomposing terpene hydrocarbons *in vacuo* they could increase the yield of isoprene. They effected this depolymerization by means of an electrically heated platinum spiral. By reducing the pressure within the apparatus to 2–3 mm. they obtained as high as 60% yield of very pure isoprene. In the older pyrogenetic decompositions of turpentine, where the reaction was carried out at ordinary pressures, the "isoprene" contained appreciable amounts of trimethylethylene.

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[1] The boiling point of isoprene dibromide is 92° at 12 mm.; 105° at 20 mm.; 119° at 42 mm

[2] *Ann.*, 383, 229 (1911)

[3] *Ber.*, 44, 2212 (1911).

The above consideration led me to study the effect of reduced pressure on the catalysis of the oxide. The results were found to agree with the expectation.

Experiment II.—Ninety-nine grams of methylbutyleneoxide were slowly distilled through a glass tube containing freshly prepared and ignited pieces of kaolin. The latter filled the tube over a length of 60 cm. The temperature of reaction was kept at 440–460°. The pressure within the apparatus was reduced to about 60 mm. The decomposition products were passed first through a receiver cooled with ice water, and the low boiling liquids condensed in a second receiver cooled with a mixture of solid carbon dioxide and ether. The water formed from the dehydration amounted to 18 cc., which is equivalent to 86 g. of the oxide. The organic substances were dried and fractioned through a column. Forty-nine g. of the substance boiled below 45°, mostly at 33–38°, 12 g. of the oxide were recovered as methylbutanal. The yield of the hydrocarbon fraction amounted to about 62% of the total oxide used. But, as the water of dehydration amounted to 87% of the theoretical, it is very likely that quite a little of the hydrocarbon fraction was lost, partly during the catalysis, and partly in handling it prior and during the fractionation. Considering, now, that methylbutanal also can be dehydrated to isoprene, it is quite natural to assume that the dehydration of methyl-2-butyleneoxide-1,2 can be made very nearly quantitative.

The metamerization of the oxide to the aldehyde is a function, among other things, also of the rate of catalysis; hence the slower the dehydration, within certain limits, the less will the amount of aldehyde obtained be. The catalyst in the experiment was found to have been much less carbonized than the one in the preceding experiment. This would indicate that the amount of trimethylethylene formed would be much less. This was proven to be the case by separating the two hydrocarbons by means of their dibromides, as above. Thus it was found that the mixture of the dibromides consisted over 80% of the isoprene derivative. The isoprene dibromide was dehalogenated to the hydrocarbon by Gustavson and Demjanoff's[1] zinc-dust method, and the isoprene polymerized to rubber. The purified rubber as well as the vulcanized product were found to be of good quality.

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[1] *Chem. Zentr.*, 1888, 1345.

Experiment III.—One hundred grams of the oxide were dehydrated as in the last experiment with kaolin at 450°. The pressure was kept at below 1 mm. by means of a May-Nelson rotary vacuum pump. No attempt was made to get a quantitative catalysis, as the pump leaked a little. The decomposition products were collected at ordinary pressures at the exit end of the pump. Thirty grams of the dried liquid boiled at 34–37°. The high boiling fraction consisted mostly of methylbutanal. The hydrocarbon was dried over night in presence of sodium. In the morning it was found that some of the isoprene had already solidified. The unchanged hydrocarbon was distilled into a sealing tube—the hydrocarbon showed an absolutely constant boiling point of 35–36°. The liquid was treated with 1–2 g. of sodium wire, and after sealing the tube, submitted to polymerization according to Harries'[1] directions. The tube was kept at 60° for two hours, and then left at room temperature over night. In the morning the contents of the tube were found solid, except a little portion on the surface, which showed signs of a slight mobility. The heating at 60° was continued for about 16 hours more. The rubber was treated according to the directions of Harries, and, after drying, weighed 12 grams. The product was very tough, and was vulcanized to a substance having more of the properties of leather than of vulcanized natural rubber. It has been observed by Harries[2] that the sodium polymerization products are not identical with the "normal" polymerization products, hence it is not surprising if the vulcanized products in this case had different physical properties.

Harries,[1] discussing the polymerization of isoprene in presence of sodium, states that the best results are obtained with the pure hydrocarbon. In this case, it can be polymerized quantitatively to a solid, rubber-like mass, on heating for 50 hours at 60°. It would seem, therefore, that the isoprene obtained in experiment 3 was as pure as could possibly be obtained, as this latter product required considerably less time to solidify than the product obtained by Harries and Gottlob from carvene on decomposing the latter by means of the "isoprene-lamp." It has been our experience that impure samples of isoprene never gave a good sample of rubber. It follows, therefore, that the hydrocarbon, obtained by the older pyrogenetic depolymerization methods of terpenes at ordinary pressures, must be separated from the accompanying trimethylethylene before it is subjected to polymerization.

Staudinger, Endle and Herold,[3] in a recent paper, discuss the pyrogenetic decomposition of butadiene hydrocarbons, and observe that isoprene, passed through a tube heated at 750°, is changed partly to tarry

[1] *Ann.*, 383, 217 (1911).

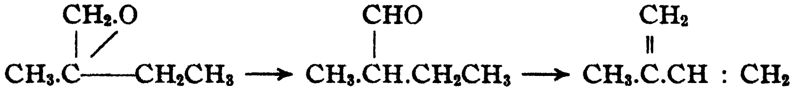
[2] *Ibid.*, 383, 210, 217, 221; 395, 221, 244, 245, 253.

[3] *Ber*, 46, 2466 (1913).

substances. The rest is broken up into gaseous products, such as butadiene, hydrogen, methane and ethylene. The formation of these is accompanied by considerable carbonization. Even at 400–500° isoprene undergoes partial change, as it was found that trimethylethylene was formed to some extent by the reduction of the isoprene. The same authors also observe that isoprene can be distilled several times over a glowing platinum spiral at 15 mm. without suffering any considerable transformation.

The conclusion from the experiments above described, and the work done by the last named authors, is that any pyrogenetic reactions for the production of isoprene or its homologues must be carried out under low pressure.

Dehydration of Methyl-1-butanal, $CH_3.CH_2.CH(CH_3).CHO$.—It has been observed that isoamylene oxide in the course of its dehydration to isoprene is partly metamerized to methylbutyraldehyde. Considering the work of Ipatieff and Leontovitch,[1] one might be led to assume that the dehydration to isoprene is a secondary process, the first being a metamerization of the oxide to the aldehyde—this taking place at about 250° in presence of a catalyst. If this assumption were true, the reactions involved would take the following course:



$$CH_3.\overset{CH_2.O}{\overset{|\,/}{C}}\!\!-\!\!-CH_2CH_3 \longrightarrow CH_3.\overset{CHO}{\overset{|}{CH}}.CH_2CH_3 \longrightarrow CH_3.\overset{CH_2}{\overset{\|}{C}}.CH : CH_2$$

The methylbutanal used was obtained by the fractionation of the crude aldehyde fractions formed in the catalysis of the oxide.

One hundred g. of the aldehyde were catalyzed as in Experiment 3. The temperature was kept at 500–550°, and the vacuum was that of the May-Nelson pump. The dried decomposition products were fractioned through a column; 10 g. of the substance boiled at 34–39°. This product was dried over sodium, and distilled into a sealing tube. It was polymerized by Harries' sodium method. The liquid took a long time to show signs of thickening, and it was only after months' standing, that it set to a rubber-like mass. This slowness of polymerization must have been due to the impurity of the hydrocarbon.

The dehydration of the aldehyde is accompanied by considerable carbonization, which soon stops the activity of the catalyst. Having attempted to dehydrate methylbutanal to isoprene a number of times, I am inclined to think that the dehydration of the oxide is a direct process, and is much easier, and gives a purer product than the aldehyde. It is also observed that the reaction with the oxide is effected at lower temperatures.

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[1] *Ber.*, 36, 2016 (1903).

Conclusions.

Oxides of the hydrocarbons can be dehydrated to the hydrocarbons of the butadiene series, at temperatures above 350° and in presence of catalysts.

The use of reduced pressures in these reactions is absolutely necessary; otherwise, the butadiene hydrocarbon suffers partial decomposition, giving rise, among other products, to hydrocarbons with one double bond. The hydrocarbons obtained with the use of high vacuum can be polymerized directly after distillation.

Methyl-1-butanal is capable of dehydration to isoprene.

In conclusion, I wish to thank my colleague, R. B. Earle, for helping me in carrying out the experiments described in this paper.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE ACTION OF HALOGEN ON 4-NITRO-*m*-CRESOL.

BY L. CHAS. RAIFORD.

Received February 10, 1914.

In their proof of the position of the chlorine atom in the stereoisomeric oximes which they obtained from para chlorotoluquinone, Kehrmann and Tichvinsky[1] started out by chlorinating 4-nitro-*m*-cresol.[2] They obtained a product which they regarded as a monochloro compound, in which they assumed that chlorine had taken a position para to methyl. Without isolating their product, they reduced it to the corresponding aminocresol, which latter they reported as identical with the monochloroaminocresol obtained by the reduction of their oximes. In addition to the fact that, in the experiments cited, the intermediate products were not isolated, proof of the position of chlorine is further lacking to the extent that the oximes were not prepared from the base obtained by reduction of the chloronitrocresol; nor was it shown that this base could be oxidized into the quinone from which the oximes were prepared. The identity of the bases obtained from the two sources was claimed solely on the fact that they melted at the same temperature, and that their acetyl derivatives had identical m. p. It is not stated whether the corresponding products were melted together or not.[3]

The present writer, working with Stieglitz, in an attempt to prepare stereoisomeric chloroimidoquinones[1] corresponding to the oximes referred to above, had occasion to repeat the work of Kehrmann and Tichvinsky on the chlorination of 4-nitro-*m*-cresol. In doing this their directions were followed as closely as the very brief descriptions would permit, except that all products were isolated, purified and analyzed. In this way it was proved conclusively[2] that chlorine must have persistently entered chiefly into the position ortho to methyl, that is, between methyl and hydroxyl, thus giving 2-chloro-4-nitro-*m*-cresol.

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[1] *Ann.*, 303, 20 (1898).

[2] *Ibid.*, 217, 52 (1883).

[3] I have recently found that 6-chloro-4-amino-*m*-cresol (OH = 1), the base obtained by the reduction of Kehrmann's oximes, in the condition in which he obtained it, m. p. 206–207°, may be melted with 5-chloro-4-amino-*o*-cresol, m. p. 205–206°, without depression. This indicates that it would be unsafe to assume the identity of two products, in this class, at least, without evidence other than that obtained by melting them together.

More recently, in preparing starting material for other work (now in progress) involving 2-chloro-4-nitro-*m*-cresol, it was decided to repeat the chlorination of 4-nitro-*m*-cresol in accordance with Kehrmann's method. The experiments were conducted by leading chlorine, diluted with an indifferent gas,[3] into an acetic acid solution of the nitrocresol, and also by using pure chlorine. Several portions were chlorinated in both ways, but in all instances the conclusions reached through the previous work were confirmed.

In order to secure the chlorinated product from these experiments, the reaction mixture (glacial acetic acid solution) was poured into water, which at once precipitated the product. The yield obtained in this way was fairly satisfactory (about 75% of the theory). and the material remaining in the filtrate was not, in the previous work, recovered. To decide, definitely, in the repetition of these experiments, whether any of the 6-chloro-4-nitro-*m*-cresol reported by Kehrmann was formed, the material in the filtrate was recovered and examined. In this way there was obtained a small quantity (about 5% of the amount theoretically possible)[4] of a monochloronitrocresol that melted at 143–144°,[5] and that turned out to be 6-chloro-4-nitro-*m*-cresol.

The position of chlorine in this compound was established by reducing it to the corresponding chloroaminocresol, and by showing that the latter is identical[6] with 6-chloro-4-amino-*m*-cresol, which was obtained by reduction of Kehrmann's oximes, and whose structure has been conclusively proved.[1]

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[1] *Am Chem. J*, **46**, 439 (1911).

[2] *Ibid.*, p. 439.

[3] Carbon dioxide was used.

[4] As this product is to be used in another investigation that has already been outlined, the conditions under which the yield can be increased will be made the subject of further study.

[5] It will be shown below that this compound is not identical with 2,6-dichloro-4-nitro-*m*-cresol, which melts at 143° with decomposition, and which was first prepared in the course of this work.

[6] Identity was not assumed on the basis of identical m. ps. for a single pair of substances alone, nor upon the failure of this pair, when melted together, to depress each other's m. p. The proof was regarded as certain only when, in addition to the behavior of the amines, two derivatives of each had been compared, and had failed to depress each other's melting point. In this case, also, the two products thought to be identical were separately melted with a third different, but closely re-

As only a very small quantity of 6-chloro-4-nitro-*m*-cresol was obtained by Kehrmann and Tichvinsky's method, it was decided to chlorinate 4-nitro-*m*-cresol in some other way. Accordingly, Kollrepp's[2] experiment was tried. This, as will be shown in the experimental part, gave nothing but 2,6-dichloro-4-nitro-*m*-cresol, although in the first experiments the amounts of the various materials used were those required by a monochloro compound. That the two chlorine atoms had taken positions 2 and 6 was shown by the fact that the dichloroaminocresol, obtained by reduction of the nitro compound under consideration, was easily oxidized to 2,6-dichlorotoluquinone, the structure of which is known.[3] The nitro compound was further identified by the preparation of several of its derivatives.

In connection with the work described in this paper, the behavior of chloroimidoquinones toward reducing agents is being studied. The experiments that have thus far been made indicate that, in at least some cases, those compounds having two chlorine atoms in the ring behave in a very different manner from the corresponding compounds having two bromine atoms similarly placed. It seemed a matter of interest, therefore, to test a chloroimide containing two different halogens attached to the ring. To secure such a compound, the start was made by preparing a bromine derivative of 2-chloro-4-nitro-*m*-cresol, by treatment of the latter with bromine in accordance with the method of Ling.[4] This gave 2-chloro-6-bromo-4-nitro-*m*-cresol, which was reduced to the amine, and the latter oxidized with hypochlorous acid in the usual way. This gave 2-chloro-6-bromo-3-methyl-4-chloroimidoquinone, while a portion of the material lost its nitrogen and was converted into the corresponding quinone (see experimental part), 2-chloro-6-bromo-3-methylquinone.

Experimental.

The starting point in this work was *m*-cresol, which was obtained by fractionating Kahlbaum's purest product. The fraction boiling at 199–200° (uncorr.) was nitrated, in fifty-gram lots, in accordance with the method of Staedel and Kolb,[5] and the isomeric nitro products that resulted were separated by distillation with steam. The para compound, which is not volatile under these conditions, and which was obtained in

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lated, substance, and only when the two mixtures behaved exactly alike were the original products regarded as identical. This precaution was taken because of the behavior of the amines mentioned above.

[1] Raiford, *Am. Chem. J*, **46**, 441 (1911).

[2] *Ann.*, **234**, 3 (1886)

[3] Raiford, *Am. Chem. J.*, **46**, 425 (1911).

[4] *J. Chem. Soc.*, **55**, 57 (1889)

[5] *Ann. Chem. (Liebig)*, **259**, 210 (1890).

crude form by allowing the distillation residue to cool, was further purified by repeated crystallization of its sodium salt from water. These crystals were then decomposed by treatment of their aqueous solution with dilute hydrochloric acid, and the free nitrocresol subsequently crystallized from hot water, from which it separated in nearly colorless crystals melting at 127–129°.

The Action of Chlorine on 4-Nitro-m-cresol.—A portion of the nitrocresol described above, weighing 10 g., was dissolved in eight times its weight of glacial acetic acid, and chlorinated in the way indicated by Kehrmann and Tichvinsky.[1] The solid that separated when the reaction mixture was poured into water was purified, and was found to have the same m. p., 133°, and other properties reported by Raiford[2] for this compound, which was shown to have the structure 2-chloro-4-nitro-*m*-cresol. The filtrate left after removing this product, as stated, was extracted with ether, and the ether removed by evaporation on a water bath. The residue was then heated in an open vessel until all acetic acid had been removed, after which the remaining solid was repeatedly crystallized from benzene until the m. p. was constant. In this way colorless, feathery crystals, radiating from a common center, were obtained. The substance is readily soluble in alcohol, chloroform and other organic solvents, but crystallizes best from benzene. It melts at 143–144° without decomposition.[3] It was at first thought that this material might be but a purer sample of 2-chloro-4-nitro-*m*-cresol, m. p. 133°, but this was shown not to be the case, by melting the two products together. The mixture melted at 108–118°. Analysis for chlorine indicated a monochloro compound.

0.1085 g. subs. gave 0.0824 g. AgCl. Calc. for $C_7H_6O_3NCl$: Cl, 18.90, found 18.77.

In order to decide the position of chlorine in this new[4] substance, a portion of it was reduced to the corresponding aminohydrochloride, from which, by treatment with ammonium carbonate solution, the free base was obtained. This was repeatedly crystallized from alcohol, from which it separated in nearly colorless scales that melted with decomposition at 223–225°. A mixture of this substance .with the chloroaminocresol[5] obtained by the reduction of Kehrmann's stereoisomeric oximes, the structure of which I have shown[1] to be 6-chloro-4-amino-*m*-cresol, melts at the same temperature as either of them separately, which indicates that they are identical. To make the case certain,[2] a portion of the base was converted into the acetyl derivative by heating it with anhydrous sodium acetate and acetic anhydride. After three crystallizations from benzene, the product melted at 163°. When mixed with the acetyl derivative of the base secured by reducing Kehrmann's oximes, the mixture still melted at 163°. To show that the new product could not be an impure sample of the acetyl derivative obtained from 2-chloro-4-amino-*m*-cresol (which melts at 178°), the product in question was melted with the latter. The mixture melted at 140–149°, which is exactly the behavior[3] shown when the acetyl derivative obtained directly from Kehrmann's oximes is used in place of the product now being identified. Finally, a portion of the base under consideration was dissolved in very dilute hydrochloric acid, and a solution of ferric chloride added. After standing half an hour the mixture was distilled with steam. There was obtained a quinone that melted at 104–105°, and which did not depress the m. p., 105°, of para-chlorotoluquinone, from which Kehrmann prepared his oximes. These facts confirm the opinion tentatively expressed at the conclusion of the previous work,[4] to the effect that when 4-nitro-*m*-cresol is chlorinated in the manner indicated the isomers, 2-chloro-4-nitro-*m*-cresol and 6-chloro-4-nitro-*m*-cresol, are formed. The reaction may be expressed as follows:

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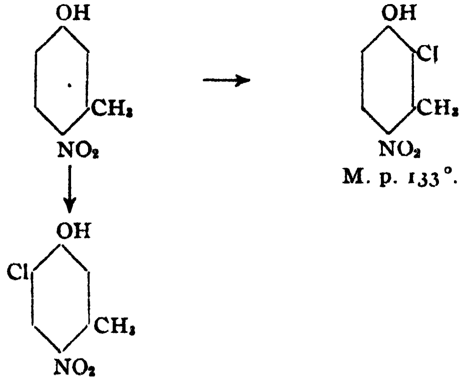
[1] *Am. Chem.* (*Liebig*), **303**, 23 (1898).

[2] *Am Chem. J.*, **46**, 448 (1911).

[3] It will be shown below that 2,6-dichloro-4-nitro-*m*-cresol melts at 143°, with decomposition.

[4] This compound was not isolated by Kehrmann, and though he reported derivatives of it, and assumed that chlorine occupied a position para to methyl in these derivatives, his proof of structure was not conclusive.

[5] Kehrmann and Tichvinsky, *loc. cit.*, reported the m. p. of this compound as 204–205°, but it does not appear that they recrystallized their material. In repeating their work I obtained the m. p. 206–207° for this base before recrystallizing it. After recrystallization it melted with decomposition at 223–225°.



M. p. 133°.

M p. 143–144°.

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[1] *Am. Chem. J.*, 46, 441 (1911)

[2] This precaution was taken because the author has recently obtained evidence that, in this class of compounds at least, different substances may be melted together without depressing each other's m. p.

[3] *Am. Chem. J.*, 46, 449 (1911).

[4] *Ibid.*, 456 (1911).

2,6-Dichloro-4-nitro-m-cresol.—Five g. of 4-nitro-*m*-cresol were dissolved, as nearly as possible, by heating it under a reflux condenser with 250 cc. concentrated hydrochloric acid; then the liquid was shaken until it reached the room temperature. A mass of small crystals separated. To this mixture there was added, in the manner described by Kollrepp,[1] the quantity of potassium chlorate solution required by the theory to convert all the nitrocresol present into the monochloro derivative. When the reaction was complete the solid was collected on a filter, washed with cold water and dried on a clay plate. The crude product melted with decomposition at 138–140°, which indicated at once that the substance could not be 2-chloro-4-nitro-*m*-cresol, melting at 133° and which has been described elsewhere.[2] The compound was found to be readily soluble in alcohol, chloroform, and benzene. It was purified by crystallization from benzene, from which it formed colorless prisms, that melt at 143° with decomposition. That this compound was not identical with 6-chloro-4-nitro-*m*-cresol, m. p. 143–144°, described above, was shown both by melting the two together, and by analysis for chlorine. A mixture of the two substances melts at 115–120°, and analysis for halogen shows the present substance to be a dichloro compound.

0.2909 g. subs. gave 0.3724 g. AgCl. Calc. for $C_7H_5O_3NCl_2$: Cl, 31.95; found. 31 65.

In view of the analysis recorded above, and of the fact that in the preparation of the compound the amounts of the various materials used were those required to give a monochloro product, the question now arose as to whether any of the latter had been formed. In order to decide this, the combined mother liquors left during the crystallization of the dichloro compound were evaporated to dryness, and the residue mixed with an excess of ammonium hydroxide solution. The ammonium salt obtained was purified by fractional crystallization. Each fraction was composed of yellow needles. Analysis of a portion of one fraction for chlorine showed that the substance was a dichloro compound.

0.1765 g. subs. gave 0.2126 g. AgCl.

Calc. for $C_7H_8O_3N_2Cl_2$: Cl, 29.68; $C_7H_9O_3N_2Cl$: 17.34; found. 29 78

When the various fractions of the above ammonium salt were separately decomposed by hydrochloric acid, the dichloronitrocresol described above, melting with decomposition at 143°, was obtained in each case.

Hydrochloride of 2,6-Dichloro-4-amino-m-cresol.—In order to further identify the dichloro product, 5 g. of the nitro compound were dissolved in 10 cc. hot alcohol, and to the boiling liquid there was added a hydrochloric acid solution of stannous chloride. From this mixture the aminohydrochloride separated, upon cooling, in nearly colorless crystals. Purification of the compound, by treatment of its hot water solution with concentrated hydrochloric acid, gave colorless crystals that no longer responded to a test for tin salt. The hydrochloride is entirely soluble in water containing a little hydrochloric acid, but does not give a clear liquid in the absence of the acid. It dissolves readily in alcohol, and in sodium hydroxide solution, giving, with the latter, a solution that rapidly becomes dark colored on standing. It is not soluble in chloroform. When heated above 250° the substance blackens and appears to decompose without melting. A portion of it was dried *in vacuo* for several days over potassium hydroxide and then analyzed for chlorine.

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[1] *Ann. Chem. (Liebig)*, **234**, 3 (1886).

[2] *Am. Chem. J.*, **46**, 447 (1911).

0.3132 g. subs. gave 0.5894 g. AgCl. Calc. for $C_7H_8ONCl_3$: Cl, 46.57; found: 46.53.

2,6-Dichloro-4-amino-m-cresol.—The hydrochloride described above was dissolved in water, to which a little hydrochloric acid had been added, and the liquid filtered. To this solution there was added slightly more than the theoretically required amount of ammonium carbonate solution. The free amine, which was promptly precipitated, was at once collected on a filter, washed several times with cold water, and dried on clay plate. In this condition the compound melted with blackening and apparent decomposition at 174°. After crystallization from benzene it gave masses of interlaced needles, that melted with blackening at 175–176°.[1] The substance is readily soluble in alcohol and in chloroform, and but sparingly soluble in ligroin.

0.1702 g. subs. gave 0.2542 g. AgCl. Calc. for $C_7H_7ONCl_2$: Cl, 36.95; found: 36.92.

2,6-Dichloro-4-acetylamino-m-cresol.—A portion of the amine under consideration was converted into an acetyl derivative by mixing it with slightly more than the theoretically required amount of acetic anhydride to convert it into a diacetyl compound, along with some anhydrous sodium acetate. The reaction began at once, with the evolution of considerable heat. The mixture was boiled for a few minutes, and then allowed to cool, when it solidified. It is soluble in chloroform, benzene, and alcohol, but was best crystallized by treatment of its alcoholic solution with water. It gave colorless needles that melted at 204–207°.[2] It is readily soluble in solution of sodium hydroxide, which indicated a monoacetyl derivative. Analysis for chlorine confirmed this view.

0.1030 g. subs. gave 0.1232 g. AgCl. Calc. for $C_9H_9O_2NCl_2$ Cl, 30.31; found: 29.57.

Oxidation of 2,6-Dichloro-4-amino-m-cresol.—A portion of the amine, weighing 1.5 g. was rubbed into a thin paste with a mixture of 2 cc. concentrated sulfuric acid and 65 cc. water. This paste was cooled to about 0°, and to it was slowly added, with shaking, a cold solution of sodium dichromate and sulfuric acid, after which the whole was allowed to stand for half an hour. The quinone that formed was removed by filtration, washed repeatedly with cold water, and dried. It melted quite sharply at 103°. This product is probably identical with the dichlorotoluquinone prepared by Claus and Schweitzer[1] from what they reported as dichloro-*m*-cresol,[2] as well as with the product previously obtained by Southworth[3] by the treatment of *m*-cresol with hydrochloric acid and potassium chlorate. When the product under consideration here was melted with the dichlorotoluquinone in which Raiford[4] has shown that chlorine is in positions 2 and 6, the melting point was still 103°. The hydroquinone obtained from the present material was found to be identical with the hydroquinone prepared from 2,6-dichlorotoluquinone.[5]

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[1] It should be noted that this compound melts at the same point as 2,6-dibromo-4-amino-*m*-cresol (*Am. Chem. J.*, **46**, 428 (1911)). A mixture of the two compounds melts to a black mass at 168–171°, which is but a very trifling depression.

[2] The quantity available was too small for further crystallization, therefore, the final product was not entirely pure. This was indicated both by m. p. and analysis.

2,6-Dichloro-4-chloroimidotoluquinone, $\overset{1}{O} : C_6HCl_2\overset{3}{(CH_3)} : \overset{4}{NCl}$.—To prepare this compound, 4 g. of the hydrochloride of 2,6-dichloro-4-amino-*m*-cresol were dissolved in water to which a few drops of hydrochloric acid had been added, the solution cooled to about 0°, and then allowed to flow in drops into an acidified (HCl) solution of sodium hypochlorite,[6] in which pieces of ice were floating. A yellow solid separated at once. The reaction mixture was allowed to stand for half an hour, after which the solid was collected on a filter, washed with cold water until the odor of hypochlorous acid was no longer noted, and then dried in the air. In this condition the substance melted at 87°, and repeated crystallization did not change this. It was a matter of interest to note that this compound melts at the same temperature as 6-chloroimido-2-chlorotoluquinone,[7] obtained by starting with the same nitrocresol used in this work. That the products were not identical was shown by the fact that a mixture of the two melts lower than either of them separately, at 57–69°, and by analysis. The substance is soluble in alcohol, chloroform, and ligroin, and may be crystallized from either liquid, though alcohol seemed to give best results. It was obtained in the form of yellow prisms.

0.2123 g. subs. gave 0.4061 g. AgCl. Calc. for $C_7H_4ONCl_3$: Cl, 47.41; found: 47.29.

The chloroimidoquinones here described were prepared in order to secure material to be used in the study of the behavior of these compounds toward reducing agents. Preliminary experiments have shown that the reaction of the 2,6-dichloro-4-chloroimidotoluquinone described above is, in this respect, in marked contrast to that of the corresponding dibromo compound previously described by Raiford.[1] In order to study the action further, with the hope of learning, if possible, to what extent this behavior varies with the presence of various halogens, it was decided to prepare a chloroimidotoluquinone with two different halogen atoms attached to the ring. This was done through the compounds specified below.

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[1] *Ber.*, **19**, 931 (1886).

[2] See Crowther and McCombie, *J. Chem. Soc.*, **103**, 542 (1913).

[3] *Ann. Chem. (Liebig)*, **168**, 270 (1873).

[4] *Am. Chem. J.*, **46**, 425 (1911).

[5] *Loc. cit.*

[6] Graebe, *Ber.*, **35**, 43, 2753 (1902)

[7] *Am. Chem. J.*, **46**, 451 (1911).

2-Chloro-6-bromo-4-nitro-m-cresol.—A portion of 2-chloro-4-nitro-*m*-cresol, weighing 3.3 g., was dissolved in 30 cc. glacial acetic acid, and to this there was gradually added from a tap funnel a solution of 0.9 cc. (one mol) bromine dissolved in 7.5 cc. of acid. The mixture became warm, and was allowed to stand over night, during which time nearly colorless crystals, weighing 1.2 g., and melting at about 150°, with decomposition, separated out. These were removed by filtration, the filtrate was poured into six volumes of cold water, and the precipitate allowed to settle. After being collected on a filter and dried on a clay plate, this material weighed 3 g., and melted with decompositon at about 150°. It was found to be identical with the crystalline material mentioned above. The united product was twice crystallized from benzene, which gave nearly colorless prisms, still melting at 150° with decomposition. The compound dissolves readily in alcohol, but sparingly in ligroin.

0.4676 g. subs. gave 0.5796 g AgHal. Calc. for $C_7H_5O_3NClBr$: Halogen, 43.33; found 43.20.

Hydrochloride of 2-Chloro-6-bromo-4-amino-m-cresol.—A portion of the nitro compound, described above, was reduced to the corresponding aminohydrochloride by treatment of its hot alcoholic solution with hydrochloric acid solution of stannous chloride. The nearly colorless product was purified in the manner already stated, until it gave no reaction for tin compounds. It shows the same general properties stated for the corresponding dichloro compound. The purified substance was dried *in vacuo* over potassium hydroxide for several days, and then analyzed for halogen.

0.2132 g. subs. gave 0.3665 g. AgHal. Calc. for $C_7H_8ONCl_2Br$: Halogen, 55.28; found. 54.69.

2-Chloro-6-bromo-4-amino-m-cresol.—A portion of the aminohydrochloride was dissolved in acidulated (HCl) water, and to this there was added a slight excess of ammonium carbonate solution. The nearly colorless precipitate that formed was at once collected on a filter, washed with three or four small portions of cold water, and dried. In this form it melted, with blackening, at 186–187°, and was practically pure. After crystallization from benzene, in which it is but very sparingly soluble and from which it separated in colorless, transparent, rhombic crystals, it melted at 187°, with decomposition.

0.2312 g. subs. gave 3233 g. AgHal. Calc. for $C_7H_7ONClBr$: Halogen, 48.82; found 48.70.

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[1] *Am. Chem. J.*, **46**, 426 (1911).

2-Chloro-6-bromo-3-methylquinone, $\overset{1}{O} : C_6H\overset{2}{Cl}\overset{6}{Br}(\overset{3}{CH_3}) : \overset{4}{O}$.—This compound was prepared by oxidation of the hydrochloride mentioned above. Three grams of the latter were rubbed into a thin paste with a mixture of 6 cc. concentrated sulfuric acid and 100 cc. water, and the whole cooled to about 0°. To this there was gradually added, with shaking, a cooled solution of sulfuric acid and sodium dichromate. The resulting mixture was allowed to stand for half an hour, then the yellow solid was removed by filtration, and washed several times with cold water. After being dried on clay plate this quinone weighed 2.5 g., which corresponds to about 97% of the theory—an unusually high yield for a quinone. The melting point of the material at this stage was 114–116°. It was found to be soluble in alcohol, chloroform, and ligroin, and was easily purified by distillation with steam or by crystallization from ligroin (b. p. 70–80°). Yellow scales of irregular shape, melting at 119°, were formed.

0.1904 g. subs. gave 0.2696 g. AgHal Calc. for $C_7H_4O_2ClBr$: Halogen, 49 03; found: 49.35.

2-Chloro-6-bromo-3-methylhydroquinone, $\overset{1}{HO}.C_6H\overset{2}{Cl}\overset{6}{Br}(\overset{3}{CH_3}).\overset{4}{OH}$.—A portion of the quinone just described was rubbed to a thin paste with water, and the mixture saturated with sulfur dioxide. After standing for some hours the liquid was heated to the boiling point, and enough water gradually added, while the boiling was continued, to dissolve all solid. After filtration the liquid was again saturated with sulfur dioxide, and the flask set aside to cool. The hydroquinone settled out rapidly in colorless crystals. By recrystallization in the same manner, a substance that melted sharply at 163° was obtained. It may also be crystallized from ligroin. When brought in contact with sodium hydroxide solution, it gives first a green color, and goes into solution to form a brownish liquid.

0.1980 g. subs. gave 0.2768 g. AgHal. Calc. for $C_7H_6O_2ClBr$: Halogen, 48 62; found: 48.72.

2-Chloro-6-bromo-3-methyl-4-chloroimidoquinone, $\overset{1}{O}:C_6H\overset{2}{Cl}\overset{6}{Br}(\overset{3}{CH_3}):\overset{4}{NCl}$.—To prepare this substance, 2.2 g. of the hydrochloride of 2-chloro-6-bromo-4-amino-*m*-cresol were dissolved in 100 cc. water with the help of a little hydrochloric acid. This solution was cooled to about 0°, and was then dropped into an acidified (HCl) solution of sodium hypochlorite which was surrounded by ice, and in which pieces of ice were floating. A yellow solid was at once formed, and this appeared to be distributed through the entire liquid in the form of an emulsion. The mixture was allowed to stand for half an hour, during which the solid settled, and the supernatant liquid became entirely clear. The chloroimide was collected on a filter, washed with cold water until the odor of hypochlorous acid had disappeared, and dried. The yield was nearly quantitative. In this state the material began to shrivel between 85 and 90°, and melted at 90-92°. It may be purified by crystallization from alcohol, from which the chloroimide separates in the form of square prisms that melt at 93-94°. From ligroin (b. p. 70-80°), it gives crystals of the same shape, melting at the same temperature. It decomposes suddenly, with charring, when heated above 176°.

0.3443 g. subs. gave 0.6079 g. AgHal. Calc. for $C_7H_4ONCl_2Br$: Halogen, 56.12; found: 56.14.

The mother liquor, left after crystallization of the above described chloroimidoquinone, was evaporated to a small volume and allowed to cool. The solid that separated melted at 111-113°, which showed that this material could not be the chloroimide. Further crystallization from alcohol raised the m. p. to 114-115°, but the small quantity of material available made it impossible to secure a product that was entirely pure. The substance crystallized in the form of the irregular scales characteristic of 2-chloro-6-bromo-3-methylquinone described above. A mixture of a pure sample of the latter, m. p. 119°, and the product here in question, melted at 115-119°, showing no depression. When the substance to be identified was mixed with a pure sample of 2-chloro-6-bromo-3-methyl-4-chloroimidoquinone, m. p. 93-94°, both of which were produced in the same experiment, the mixture melted at 75-86°. Analysis for halogen gave too high a value, which suggests a trace of a higher halogenated product.

0.0785 g. subs. gave 0.1130 g. AgHal. Calc. for $C_7H_4O_2ClBr$: Halogen, 49.03; found: 50.06.

Summary.

1. When 4-nitro-*m*-cresol is chlorinated by passing pure or diluted chlorine into an acetic acid solution of the substance, a mixture of 2-chloro-4-nitro-*m*-cresol and 6-chloro-4-nitro-*m*-cresol, in which the first is present in largest amount, is formed.

2. When 4-nitro-*m*-cresol is chlorinated by means of a mixture giving so-called nascent chlorine, nothing but 2,6-dichloro-4-nitro-*m*-cresol is obtained.

CHICAGO, ILL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

TETRACHLOROFLUORESCEIN AND SOME OF ITS DERIVATIVES.

BY W. R. ORNDORFF AND E. F. HITCH.

Received February 10, 1914.

Historical.

Tetrachlorofluorescein was first prepared by Graebe[1] in the course of his investigation of tetrachlorophthalic acid. It was made by heating to 200° thirteen parts of tetrachlorophthalic acid anhydride with ten parts of resorcinol for 2 or 3 hours. The red fused mass was thoroughly extracted with boiling water, and there was left a substance which had the same yellowish red color as fluorescein. To this compound he assigned the formula:

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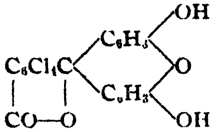
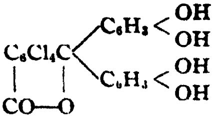
[1] *Ann. der Chemie*, 238, 333 (1887).



Graebe states that this compound, when dissolved in ammonia or sodium carbonate, is precipitated practically unchanged from these solutions by an acid, and it makes no difference whether the solution be made by warming or at ordinary temperature. When, however, the tetrachlorofluorescein was dissolved in caustic soda, either cold or hot, and then precipitated by an acid, a product was obtained containing one molecule of water more than the tetrachlorofluorescein itself, which did not lose this molecule of water even when heated for some time to 100°, and also differed in its properties from tetrachlorofluorescein. This compound, which he calls tetrachloro-orthofluorescein, or tetrachlorofluorescein hydrate, is given the following formula:



and is regarded by Graebe as derived from the unstable form of fluorescein having the composition $C_{20}H_{14}O_6$, which Baeyer[1] mentions in his work on the phthaleins. Tetrachloro-orthofluorescein is insoluble in water, only slightly soluble in alcohol but easily soluble in ether. From the last solvent it crystallizes in reddish yellow needles. It is precipitated from solution in the alkalies by an acid in the form of pure yellow microscopic needles. It dissolves in alkalies with almost the same color and the same fluorescence as fluorescein, a difference is only perceptible when the solutions are observed in very thin layers, the solution of tetrachloro-orthofluorescein then appears red, while that of fluorescein is yellow. Tetrachloro-orthofluorescein is not changed by boiling with water, hence it is obtained having the same composition, no matter whether the alkaline solution be precipitated hot or cold. The air-dried compound loses no weight at 100°, even at 150–160° it scarcely changes. When heated, however, to 180–200° it turns red and goes over into tetrachlorofluorescein. Analyses of the tetrachloro-orthofluorescein dried at 100° are given, which agree very well with the formula $C_{20}Cl_4H_{10}O_6$. When heated with acetic anhydride it gives the same diacetyltetrachlorofluorescein as tetrachlorofluorescein itself.

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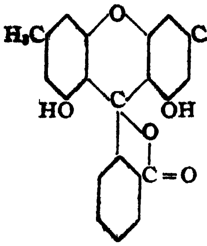
[1] *Ann.*, 183, 5 (1876).

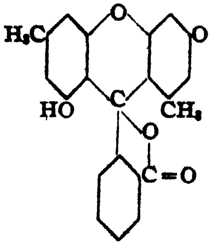
Tetrachlorofluorescein is the product which is formed on heating tetrachlorophthalic acid anhydride with resorcinol. If the fused mass be extracted with ammonia or sodium carbonate and this solution be acidified, tetrachlorofluorescein is precipitated. Longer continued action of a larger excess of ammonia or sodium carbonate results in the formation of some tetrachloro-orthofluorescein also. From this it is formed by heating to 180–200°. It is yellowish red and separates from the above mentioned solutions on the addition of acids in the form of a yellowish red precipitate, while that of the tetrachloro-orthofluorescein is yellow. In ether tetrachlorofluorescein is practically insoluble, and in this respect it differs from the compound containing a molecule of water (tetrachloro-orthofluorescein). Two chlorine analyses of the tetrachlorofluorescein dried at 100° are given and these agree very well with the formula, $C_{20}Cl_4H_8O_5$. Analyses are also given of the diacetyl derivative of tetrachlorofluorescein and of the chloride of tetrachlorofluorescein.

Since this work of Graebe, no further investigation of tetrachlorofluorescein has been made. Recently, however, C. Mettler[1] has published a paper upon dichlorodioxybenzoylbenzoic acid and its conversion into tetrachlorofluorescein and into anthraquinone derivatives. The compound which he calls tetrachlorofluorescein, while isomeric with the tetrachlorofluorescein first prepared by Graebe, and which forms the subject of this investigation, is entirely different in structure. Tetrachlorofluorescein as named by Graebe, is the anhydride of resorcinoltetrachlorophthalein, while the compound prepared by Mettler is analogous to eosin, and is tetrachlororesorcinolphthalein anhydride.

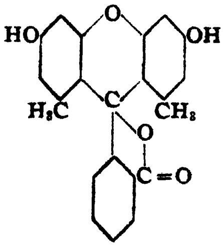
In 1896, R. Meyer and H. Meyer[2] investigated the orcinolphthaleins and found that there are three of them. They represent the structure of these compounds by the formulas:



(I)



(II)



(III)

The third formula is assigned to the isomer which fluoresces in alkaline solution on account of its great resemblance to fluorescein. It is interesting to note that they make the following statement regarding the possibility of the formation of isomers of fluorescein: "Die Tatsache, dass bei der Condensation von Phtalsäureanhydrid mit Orcin nicht nur ein Phtalein entsteht, sondern die drei structurell möglichen Isomeren nebeneinander, legt die Frage nahe, ob nicht die Bildung des Fluoresceins gleichfalls von der Entstehung der zwei ausser ihm noch denkbaren Resorcinphtaleine begleitet ist. Es liegen bisher, soweit uns bekannt, keine Tatsachen vor, welche einen Anhalt zu einer solchen Vermutung geben könnten. Auch haben einige Versuche, welche dahin zielten, die Fluoresceinbildung unter verschiedenen Bedingungen zu Studiren, stets nur Fluorescein geliefert."

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[1] *Ber.*, 45, 800 (1912).

[2] *Ibid.*, 29, 2627 (1896).

The chlorinated eosins have been known to the manufacturers of dyes for some time, but no record of scientific investigation upon tetrachloroeosin has, up to the present time, been published. In 1885 a German patent was granted to R. Gnehm of the Gesellschaft für Chemische Industrie at Basel for the preparation of the chlorinated phthalic acids to be used exclusively for making eosin dyestuffs containing chlorine. The commercial tetrachloroeosin, known to the trade as Phloxine, is the sodium salt of tetrachloroeosin, and is made from the commercial tetrachlorofluorescein by brominating.

The fluorescence of organic substances, and especially of substances chemically related to fluorescein, has been the subject of much investigation. Most of the researches in this field have been conducted with the object of ascertaining if there exists any relation between fluorescence and chemical constitution, and to determine the exact nature of such relation, if it does exist. Many theories have been advanced by chemists and physicists to explain this phenomenon, and it is generally accepted at the present time that there is a close relation between chemical structure and fluorescence. Chemists have made attempts to formulate a theory that will explain this relationship and account for all the known facts. It is not within the scope of this work to go into a discussion of the various theories of fluorescence, but those who may be interested in this field of investigation will find an excellent review of these theories given by Samuel Smiles in his book entitled "The Relations between Chemical Constitution and Some Physical Properties." The theory of Stark and Meyer and of Kauffmann, that the benzene nucleus is the seat of fluorescence of aromatic organic compounds, is generally accepted by chemists at the present time as the one which more nearly explains the facts. Chemists and physicists are beginning to realize the great importance of studying very weak fluorescence and fluorescence in the ultraviolet portion of the spectrum. Until the complete fluorescence spectra of many more substances are studied, any theory to account for this phenomenon will be inadequate.

An excellent review of the investigations that have been undertaken to determine the relationship which exists between color and constitution of the phthaleins, and other triphenylmethane derivatives, together with a statement of some of the theories advanced to account for the color of this group of compounds, is given by Orndorff and Delbridge[1] in their first paper on "Tetrachlorgallein and Some of Its Derivatives."

This investigation was undertaken for the purpose of determining what influence the introduction of four chlorine atoms into the phthalic acid part of the fluorescein molecule would have upon the chemical conduct and general properties of this phthalein; for the purpose of determining whether any of the isomeric tetrachlorofluoresceins, theoretically possible,[2] are formed; for the purpose of extending our knowledge of colored compounds and of the relation between the color and constitution of organic compounds; and finally, to throw some light, if possible, on the phenomenon of fluorescence.

Experimental.

The resorcinol used in this investigation was obtained from Merck and Company. It was perfectly white, melted at 115–116° (uncorr.), and left no residue on ignition. It dissolved completely to a clear solution in water, in alcohol, and in ether. The tetrachlorophthalic acid was obtained from the Heller and Merz Company, and was purified by the method described by Delbridge.[3] The purity of the acid was checked by determinations of the molecular weight. A weighed portion of the acid was dissolved in a measured amount of tenth-normal sodium hydroxide solution, using about 10% excess. About 0.5 cc. excess of tenth-normal hydrochloric acid was then added, the solution boiled for one minute to expel carbon dioxide, cooled, and the excess of hydrochloric acid titrated with tenth-normal sodium hydroxide, using phenoltetrachlorophthalein as the indicator.[4] The following results were obtained with the purified tetrachlorophthalic acid:[5]

Subst. 0.3890, 0.3322; cc. 0.1 N NaOH, 24.88, 21.22.

Calculated for $C_6Cl_4(CO_2H)_2.0.5H_2O$, mol. wt. 312.9; found, 312.7, 313.1

Tetrachlorofluorescein.

Preparation.—This compound was prepared by four different methods as follows: Fusion of tetrachlorophthalic acid and resorcinol with zinc chloride; fusion of tetrachlorophthalic acid and resorcinol with phosphorus pentoxide; fusion of tetrachlorophthalic acid and resorcinol; fusion of tetrachlorophthalic anhydride and resorcinol. In the first method 313 grams of tetrachlorophthalic acid (1 mol) and 231 grams of resorcinol (2.1 mols) were thoroughly mixed. To this mixture were then added 150 g. of freshly fused and finely powdered zinc chloride. After thorough grinding in a mortar, the whole was transferred to a two-liter round-bottom flask, and the flask placed in a bath of concentrated sulfuric acid containing 40% potassium sulfate. This bath was then heated to 200–210° for two hours. The mixture softened to a pasty mass and became dark red at the end of one-half hour, but at no time did the mass become completely liquefied, nor did the temperature within the flask rise above that of the bath. At the end of two hours the mass had solidified and the heating was discontinued. After cooling, the flask was broken and the hard, solid cake pulverized and extracted with hot water containing two 2% hydrochloric acid. The crude product thus obtained was dissolved in 5% sodium hydroxide solution, the solution filtered, and an excess of hydrochloric acid added. The mixture was then boiled by blowing in steam, and the red tetrachlorofluorescein filtered off while hot. The material thus obtained was washed free from hydrochloric acid, soluble chlorides, and unchanged tetrachlorophthalic acid, with hot water and dried to constant weight at 110°. This product, contrary to the statement of Graebe (see page 681), is the anhydrous tetrachlorofluorescein. Yield, 88% of the theoretical calculated from the amount of the tetrachlorophthalic acid used.

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[1] *Am. Chem. J.*, 42, 183 (1909).

[2] See page 686.

[3] *Am. Chem. J.*, 41, 414 (1909).

[4] *Ibid.*, 41, 349, 401 (1909).

International atomic weights (1914) are used in this paper.

In the second method, which was conducted in the same manner as the first, 166 g. of phosphorus pentoxide were substituted for the zinc chloride. At the end of fifteen minutes the mass had completely melted to a thin, red liquid which gradually became viscous. This change was accompanied by a considerable rise in temperature within the flask, the thermometer registering as high as 240°, or about 30° above that of the bath. At the end of an hour the mass had solidified. The heating was continued for half an hour longer to complete the reaction. The solid mass was extracted with water in the same manner as before, and washed with hot water until free from phosphoric acid. The crude material was then dissolved in 5% sodium hydroxide solution, filtered, and the filtrate acidified with 5% hydrochloric acid. The mixture was then boiled by blowing in steam, the red anhydrous tetrachlorofluorescein filtered off, washed with hot water, and dried at 110°. Yield, 90%.

In order to determine whether a condensing agent was advantageous, tetrachlorofluorescein was made by the fusion of tetrachlorophthalic acid (1 mol) and resorcinol (2 mols), without any condensing agent. It was found necessary to increase the temperature of the bath to 240°, in order that the reaction should take place readily. The mixture first became yellow, and soon changed to a thin, red liquid. This gradually became viscous, upon further heating, and at the end of an hour was of a pasty consistency. At the end of two hours the mass had completely solidified and the reaction was stopped. It was then extracted and treated in the same manner as in the fusion with phosphorus pentoxide. Yield, 85%.

In the last method of preparation, tetrachlorofluorescein was made from tetrachlorophthalic anhydride and resorcinol, following the directions of Graebe.[1] Tetrachlorophthalic anhydride (1 mol) and resorcinol (2 mols) were thoroughly mixed and heated to a temperature of 200–210°. The material changed within fifteen minutes to a light yellow pasty mass, which at the end of half an hour had become a thin, dark red liquid. This remained unchanged when the heating was continued for two hours at this temperature. The temperature of the bath was then increased to 230°. Under these conditions, the mass became solid upon heating for an hour longer. The solid cake was then extracted and treated in the same manner as before. Yield, 81%.

Purification of Tetrachlorofluorescein.—One hundred grams of the crude tetrachlorofluorescein, prepared by one of the methods previously described were dissolved in one liter of water containing 30 grams of sodium hydroxide. This solution was filtered, diluted to two liters, and poured, with constant stirring, into two liters of a solution containing 250 cc. of hydrochloric acid (sp. gr. 1.10). The orange-yellow precipitate thus obtained was extracted with ether, about two liters being required to complete the solution. A small amount of the precipitate is insoluble in the ether. This insoluble material has a very *dark red* color, and constitutes about 5% of the crude tetrachlorofluorescein. It is perhaps a mixture of the two possible isomers (see p. 723). It dissolves readily in alkalies with a deep red color and an *intense greenish fluorescence*, and is precipitated as a dark red material, probably a hydrate, upon the addition of acids to the dilute alkaline solution. This dark red material is only slightly soluble in ether, but *readily soluble in alcohol*, and hence is different from the red anhydrous tetrachlorofluorescein described below, which is practically insoluble in these solvents. The ether extract, after filtering off this insoluble material, was dried by shaking with fused calcium chloride, one-half of the ether distilled off, and an equal amount of alcohol added. The distillation was continued until orange-yellow crystals began to appear. Upon repeated recrystallization from alcohol, this substance was obtained light yellow in color with a reddish tinge. It was thought that this red color was due to a small amount of the dark red impurity remaining after the extraction with ether.[2] Since repeated crystallization from alcohol, and then from acetone, did not remove this color, the substance was converted into the diacetate by means of acetic anhydride and sodium acetate. This diacetate was crystallized from benzene until a *perfectly white product* was obtained, then saponified with alcoholic caustic potash. The alcoholic solution of the dipotassium salt thus formed was diluted with a large amount of water, and poured, with constant stirring, into an excess of dilute hydrochloric acid. The light yellow precipitate of the hydrate was then filtered off and thoroughly washed with water until free from hydrochloric acid and chlorides. This hydrate was found to be completely soluble in ether, thus showing that it contained none of the dark red material (possibly a mixture of the two isomeric modifications of tetrachlorofluorescein) present in the crude product.

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[1] *Ann.*, 238, 333 (1887).

[2] Later it was shown that the hydrate is partially converted into the red tetrachlorofluorescein by this treatment and a part of this red color was due to this substance.

When dried to constant weight at 170° in the electric drying oven[1] this hydrate was converted into a red compound which proved to be pure anhydrous tetrachlorofluorescein as shown by the following chlorine determinations:[2]

Subst. 0.1936, 0.2304, cc. 0.1 N $AgNO_3$, 16.43, 19.58

Calculated for $C_{20}H_8Cl_4O_5$, Cl, 30.18; found, 30.10, 30.14

The tetrachlorofluorescein thus obtained is a brick-red powder, soluble in alkalies with a reddish yellow color and greenish fluorescence. If the alkaline solution be diluted with a large amount of water, the color becomes pinkish yellow with the same greenish fluorescence. The fluorescence is much less marked than in the case of fluorescein. It is insoluble in water, acetone, ethyl acetate, ether, and chloroform, very slightly soluble in 95% alcohol with a yellow color and greenish fluorescence.

Later it was found that the above described method of purification by dissolving the hydrate in ether and recrystallizing from alcohol and from acetone is unnecessary, since the crude product can be converted directly into the diacetate, and this diacetate obtained perfectly white and pure by repeated crystallization from benzene or from acetone. This diacetate has the same melting point and other physical constants as the diacetate prepared from the previously purified tetrachlorofluorescein. When this white product is saponified with alcoholic caustic potash, and the diluted alcoholic solution acidified, a yellow hydrate is formed which, when filtered off and thoroughly washed with water, was found to be completely soluble in ether, showing that it contains none of the dark red material supposed to be a mixture of the isomeric tetrachlorofluoresceins. *All* of the tetrachlorofluorescein used in this investigation was purified by converting the more or less impure tetrachlorofluorescein into the diacetate, recrystallizing this diacetate from a number of solvents until it was perfectly white and had a constant melting point, and saponifying it with alcoholic caustic potash. In this manner a tetrachlorofluorescein was obtained free from any of the possible isomeric tetrachlorofluoresceins.

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[1] *Am. Chem. J.*, 48, 477 (1912).

[2] All the chlorine determinations in this article were made by the lime method. *Am. Chem. J.*, 41, 393.

Tetrachlorofluorescein Hydrate.—When a very dilute alkaline solution of pure tetrachlorofluorescein is poured into an excess of dilute mineral acid, a light yellow substance is precipitated. This material was prepared for analysis and investigation in the following manner: Ten grams of pure tetrachlorofluorescein, obtained from the saponification of the pure diacetate, (see p. 691), were dissolved in 500 cc. of water containing 3 g. of potassium hydroxide. After filtering, this solution was diluted to one liter and poured slowly and with constant stirring into a liter of water containing 3 g. of hydrochloric acid gas. The light yellow precipitate thus formed was filtered off on a Buchner funnel, transferred to a flask, washed thoroughly by shaking with water, again filtered and washed on the funnel, until the wash water gave no test for chlorides. This yellow substance was dried in the air and analyzed. When heated in the electric drying oven to a temperature of 110° the substance lost weight, moisture collected upon the cool part of the tube,[1] the material turned red and came to constant weight in *forty-five minutes*. The following results show that this substance is a hydrate of tetrachlorofluorescein:

Subst. 0.2554, 0.2356; loss at 110°, 0.0103, 0.0088
Calculated for $C_{20}H_8Cl_4O_5.H_2O$, 3.69; found, 4.03, 3 74

When this hydrate is allowed to stand in the air (temperature 23–25°) for ten days some of the combined water is lost, as shown by the following determination:

Subst. 0.5537, loss at 110°, 0.0159 = 2.87

This is also shown by the fact that the material dried for this length of time is *not completely* soluble in ether—some dark red material, anhydrous tetrachlorofluorescein, remaining undissolved—whereas the freshly prepared *dry* hydrate is *completely* soluble in ether.

The following chlorine determinations on the product, dried to constant weight at 110°, show that it is the red anhydrous tetrachlorofluorescein:

Subst. 0.2429, 0.1133; cc. 0 1 *N* $AgNO_3$, 20.68, 9.66
Calculated for $C_{20}H_8Cl_4O_5$, Cl, 30.18; found, 30.20, 30.23

Tetrachlorofluorescein hydrate is very soluble in ether, acetone, and ethyl acetate, readily soluble in methyl and in ethyl alcohol, only slightly soluble in chloroform, and insoluble in benzene. When the moist hydrate is crystallized from 95% ethyl alcohol, the excess of the solvent being distilled off below 35° (under reduced pressure), it is almost completely converted into the carbinol acid (see p. 690), which forms beautiful pale yellow needles.

The yellow hydrate also loses a molecule of water when kept in an evacuated desiccator over phosphorus pentoxide, but in this case the anhydrous product has only a pale yellow color, and is probably the lactoid form of tetrachlorofluorescein, which was also obtained from the etherate and from the compound with ethyl acetate (see pp. 694 and 695). The change into the red tetrachlorofluorescein is also brought about by boiling the yellow hydrate with water, contrary to Graebe, or with benzene. Attempts to recrystallize the yellow hydrate by distilling off some of the solvent at *atmospheric pressure* always resulted in a mixture of crystals of the yellow hydrate, or carbinol acid, and the red tetrachlorofluorescein. The yellow hydrate when acetylated with acetic anhydride gives the same diacetate as is obtained from the red anhydrous tetrachlorofluorescein and from the carbinol acid. The yellow hydrate dissolves in solutions of the alkalies with the same color and fluorescence as tetrachlorofluorescein itself, and it is precipitated out again when the dilute alkaline solution is poured into an excess of acid. The yellow hydrate is also formed, contrary to the statement of Graebe, when a dilute solution of tetrachlorofluorescein in ammonia or sodium carbonate is precipitated by acid.

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[1] *Am. Chem. J.*, **41**, 404 (1909) and **48**, 477 (1912).

Acetonate of Tetrachlorofluorescein. The hydrate dissolves in acetone with a clear yellow color, and when some of the solvent is distilled off light yellow crystals separate. These may be obtained almost white upon recrystallization from the same solvent. When this substance is heated to 160° in a current of carbon dioxide, both water and acetone are given off. The material was analyzed in the following manner: A weighed amount was placed in a platinum boat, inserted in the electric drying oven[1] and heated to a temperature of 160°. The tube was connected to two Hugershoff gas wash bottles containing distilled water and surrounded by ice. A current of dry carbon dioxide was passed over the heated substance, the acetone being absorbed in the water and subsequently determined by titration with standard iodine solution.[2] The following results were obtained from three different samples made at different times:

Subst. 0.4945, 0.6367, 0.4013; loss at 160°, 0.0773, 0.0856, 0.0578

Calculated for loss of acetone and water from $C_{20}H_8Cl_4O_5.C_3H_6O.H_2O$, 13.93, found, 15.63, 13.44, 14.40

The solution in the two Hugershoff wash bottles of Determination I was made up to 500 cc. with distilled water, and three 50 cc. portions (*a*, *b*, *c*) were titrated with standard iodine solution. Cc. 0.1 *N* iodine, *a*, 4.89; *b*, 4.85; *c*, 4.89 Acetone found. 9.58, 9.50, 9.58; mean, 9.53.

The solution in the wash bottles in Determination II was diluted and titrated in the same manner with the following results: Cc. 0.1 *N* iodine, *a*, 6.21, *b*, 6.08; *c*, 6.20. Acetone found, 9.43, 9.24, 9.42; mean, 9.36

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[1] *Am. Chem. J.*, **48**, 477 (1912).

[2] *Ibid.*, **44**, 6 (1911).

From Determination III the following results were obtained: Cc. 0.1 *N* iodine, *a*, 3.95; *b*, 3.91. Acetone found, 9.52, 9 43; mean, 9.48. Calculated for $C_{20}H_8Cl_4O_5.C_3H_6O.H_2O$, 10.62

The compound remaining after the acetone and water are driven off is the red anhydrous tetrachlorofluorescein as shown by the following analyses:

Subst. 0.2783, 0.1738; cc. 0.1 *N* $AgNO_3$, 23.62, 14.75
Calculated for $C_{20}H_8Cl_4O_5$, Cl, 30.18; found, 30.09, 30.10

From these results it seems probable that the almost white product obtained from the acetone solution of the hydrate, is a mixture of the *di*acetonate of tetrachlorofluorescein and the hydrate itself, or it may be a mixture of the diacetonate and tetrachlorofluoresceincarbinolcarboxylic acid (see below). The fact that the compound has such a slight color indicates that it contains very little, if any, of the yellow hydrate.

Tetrachlorofluoresceincarbinolcarboxylic Acid.—This compound was made from the purified diacetate of tetrachlorofluorescein by saponifying with alcoholic sodium hydroxide, in the same manner as in the preparation of the disodium salt of tetrachlorofluorescein (see p. 698). The alcoholic solution, containing an excess of sodium hydroxide, was diluted with a large amount of water and poured into an excess of dilute hydrochloric acid. After stirring with a current of air for five minutes the precipitate was allowed to settle, the supernatant liquid poured off and the precipitate filtered off on a Buchner funnel. This precipitate was redissolved in sodium hydroxide, the solution diluted to three liters, filtered and poured slowly, and with constant stirring, into an excess of hydrochloric acid diluted to three liters. The light yellow precipitate thus formed was extracted at once with ether. The amber colored ethereal solution was separated from the aqueous layer, filtered, and dried by shaking for ten minutes with a large amount of fused calcium chloride. The solution was then filtered into a round bottom flask and one-half of the ether distilled off on the water bath. After the addition of an equal amount of absolute alcohol, the distillation was continued at 35°, under reduced pressure, until almost white crystals separated. These were filtered off, shaken with absolute alcohol, and the mixture filtered, when the material was obtained almost white, only a faint yellow color being noticeable. Some of this substance was recrystallized from absolute alcohol, under reduced pressure, but this yellow tinge remained. An attempt was made to recrystallize some of this material from methyl alcohol, under reduced pressure, but a mixture of the red anhydrous tetrachlorofluorescein and the carbinol acid was always obtained.

The air-dried material loses no weight when kept in an evacuated desiccator over phosphorus pentoxide for two weeks. When heated in a current of carbon dioxide to a temperature of 110° the carbinol acid loses water very slowly, forty-eight hours being required for all the water to be driven off. If however, the temperature be increased to 150°, the material comes to constant weight in eight hours. The loss in weight is entirely due to water, no alcohol or ether being given off. The carbinol carboxylic acid crystallizes with a half molecule of water of crystallization as shown by the following determinations of the loss in weight:

Subst. 0.6635, 0.7319; loss at 150°, 0.0360, 0.0385. Calculated for change from $C_{20}H_{10}Cl_4O_6.0.5H_2O$ to $C_{20}H_8Cl_4O_5$, 5.44; found, 5.43, 5.26

When heated to constant weight at 150°, the carbinol acid gives the red anhydrous tetrachlorofluorescein, as shown by the following chlorine determinations:

Subst. 0.2688, 0.2531; cc 0.1 *N* $AgNO_3$, 22.85, 21 45
Calculated for $C_{20}H_8Cl_4O_5$, Cl, 30.18; found, 30.14, 30.05

Tetrachlorofluoresceincarbinolcarboxylic acid is also completely changed to the red anhydrous tetrachlorofluorescein by boiling for some time with water. It is partially changed to the red anhydrous tetrachlorofluorescein when recrystallized from methyl or ethyl alcohol or from ether, when the excess of the solvent is distilled off at atmospheric pressure, or if the solutions be allowed to evaporate in the air. It can, however, be recrystallized unchanged from absolute ethyl alcohol, provided the excess of the solvent be distilled off below 35°, under reduced pressure.

It is very soluble in acetone, ethyl acetate, and ether, less soluble in methyl and ethyl alcohol, practically insoluble in chloroform and benzene. It dissolves in the alkalies and alkaline carbonates with the same color and fluorescence as the yellow hydrate of tetrachlorofluorescein, and this alkaline solution when acidified gives the same yellow hydrate as the alkaline solution of tetrachlorofluorescein does. It is thus possible to convert the carbinol acid into the yellow hydrate, and this hydrate can be reconverted into the carbinol acid by the method given above. Both the yellow hydrate and the carbinol acid give the same red anhydrous tetrachlorofluorescein when heated to 150°. This product gives the yellow hydrate when dissolved in alkalies and the solution is acidified with a mineral acid. The carbinol acid also gives the same diacetate (melting point 256°) as is obtained from the anhydrous tetrachlorofluorescein and from the hydrate (see p. 688). On standing in a stoppered bottle the carbinol acid gradually takes on a yellow color.

Tetrachlorofluorescein Diacetate.—One hundred grams of anhydrous tetrachlorofluorescein, made by heating the product recrystallized from acetone to constant weight at 140°, were mixed with 100 g. of anhydrous sodium acetate and 500 g. of pure acetic anhydride, and this mixture heated to boiling for three hours. The solution was allowed to cool, when the diacetate crystallized out and most of the sodium acetate remained in the solution. The crystals of tetrachlorofluorescein diacetate were filtered off, washed thoroughly with water and dried to constant weight at 110°. Yield, 90 g. The filtrate was poured into water and 15 g. more of the diacetate were obtained. The crude material was then dissolved in benzene and crystallized twice from this solvent. The diacetate thus obtained was perfectly white and had not the slightest trace of color. The melting point of the product dried at 160° is 256° (uncorr.). Separate portions of this product were crystallized from absolute alcohol, acetone, and ethyl acetate. The material obtained from each of these solvents had the same melting point as the original, and was, therefore, pure, as shown by the following determinations on the air dried product:

Subst. 0.7958, 1.1786; loss (benzene) at 160°, 0.0935, 0.1425
Calculated for $C_{20}H_6Cl_4O_5(CH_3CO)_2.C_6H_6$, 12.35; found, 11.75, 12.09

When crystallized from benzene the diacetate, therefore, contains one molecule of benzene of crystallization. It loses a small amount of this benzene when dried in the air.

Chlorine determinations on the product heated to constant weight at 160° gave the following results:

Subst. 0.3730, 0 2805; cc. 0.1 *N* $AgNO_3$, 26.76, 20.29
Calculated for $C_{20}H_6Cl_4O_5(COCH_3)_2$, Cl, 25.60; found, 25.44, 25.65

Tetrachlorofluorescein diacetate is soluble in acetic anhydride, benzene, acetone, ethyl acetate, and slightly soluble in alcohol. When treated with alcoholic solutions of the alkalies it undergoes saponification even in the cold, quite readily when heated to boiling. Aqueous solutions of the alkalies hydrolyze the diacetate but slightly. It dissolves in concentrated sulfuric acid with a yellow color and greenish fluorescence, probably undergoing saponification. When this solution is diluted with water a light yellow compound, the hydrate, is precipitated, which is completely soluble in ether and therefore contains none of the red impurity found in the crude material (see p. 686).

Tetrachlorofluorescein Monobenzoate.—This substance was obtained in an attempt to prepare the dibenzoate of tetrachlorofluorescein by the Baumann-Schotten reaction, *i. e.*, by the action of benzoyl chloride on a cold alkaline solution of tetrachlorofluorescein. The following method was employed: 18.8 g. of tetrachlorofluorescein were dissolved in 280 cc. of water containing 20 g. of potassium hydroxide. To this solution 22.4 g. of benzoyl chloride were added slowly and with constant stirring. Within a short time after the addition of the benzoyl chloride, the benzoate separated out as a light reddish yellow, sticky mass. This substance was separated from the solution by filtration and triturated with a 2% solution of potassium hydroxide. After filtration, the material was washed well with a 2% solution of potassium hydroxide, then with hot water until all the alkali was removed. The solid residue was then extracted with 250 cc. portions of 95% alcohol until only a faint yellow color was imparted to the extract. The residue from these extractions together with the material which crystallized out from the alcoholic extract, was then dissolved in benzene and crystallized from this solvent. The crystals first obtained were orange-yellow in color but by repeated crystallization from chloroform and again from benzene, a perfectly white compound was obtained—melting point 235°. It is soluble in absolute alcohol, in benzene, and in chloroform. It dissolves with difficulty in dilute solutions of the alkalies with a yellow color and greenish fluorescence. A light yellow substance, probably a hydrate, is precipitated from these solutions on the addition of acid. The monobenzoate is slightly soluble in sodium carbonate solution with the same color and fluorescence as the dilute alkaline solution.

The air dried product loses approximately a molecule of benzene on heating to 150°, as shown by the following results:

Subst. 1.0647, 0.4052, 0 7224, loss (benzene) at 150°, 0.1152, 0.0393, 0.0588
Calculated for $C_{20}H_7Cl_4O_5(C_7H_5O).C_6H_6$, 11.97; found, 10.82, 9.70, 8.14

Determination II was made on material which had been kept in a stoppered bottle for several weeks, while Determination III was made on some of the same material which had been kept for more than a year in a stoppered bottle.

Determinations of chlorine on the product heated to constant weight at 150° show that the compound is the monobenzoate.

Subst. 0.3601, 0.2464, 0 1788[1], cc. 0.1 *N* $AgNO_3$, 24.97, 17.06, 12.40.
Calculated for $C_{20}H_7Cl_4O_5(C_7H_5O)$, Cl, 24.71; found, 24.59, 24.55, 24.82

When this white monobenzoate is heated in a current of carbon dioxide to 150° it becomes pale yellow in color. To determine if this change in color is due to decomposition involving a loss of chlorine, a determination of chlorine was made on the air-dried product and the results calculated for the material free from benzene, the loss in weight of some of the same substance having been previously determined by heating it to a temperature of 150°.

Subst. 0.3030; subst. at 150°, computed, 0.2736; cc. 0 1 *N* $AgNO_3$, 18.94.
Calculated for $C_{20}H_7Cl_4O_5(C_7H_5O)$, Cl, 24.71; found, 24.55.

From this result it is evident that the change in color is not due to decomposition, but is probably due to a partial molecular transformation from the lactoid to the quinoid form, as was observed in the case of the lactoid form of tetrachlorofluorescein (see p. 710).

Acetyl Tetrachlorofluorescein Benzoate.[2]—Five grams of the tetrachlorofluorescein monobenzoate, prepared and purified as previously described, were boiled for two and one-half hours with 25 cc. of acetic anhydride. The solution thus obtained was poured while still hot into one liter of water and the mixture allowed to stand over night. The white substance that separated out was filtered off, washed thoroughly with water, and crystallized from a mixture of ethyl acetate and ethyl alcohol. The pure white compound thus obtained was analyzed for chlorine and the following results obtained on the product heated to constant weight at 110°:

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[1] This tetrachlorofluorescein monobenzoate was made and analyzed by Mr. Wm. F. Flynn.

[2] This compound was prepared and analyzed by Mr. Wm. F Flynn.

Subst. 0.1329. 0.1577; cc. 0 1 N $AgNO_3$, 8.59, 10.21

Calculated for $C_{20}H_6Cl_4O_5(C_7H_6O)(C_2H_3O)$, Cl, 23.03; found, 22.92, 22.96

Acetyl tetrachlorofluorescein benzoate is very soluble in ethyl acetate and in benzene, only slightly soluble in alcohol. It is insoluble in aqueous solutions of the alkalies, and undergoes slight hydrolysis when boiled with these solutions. It is readily saponified by alcoholic solutions of the caustic alkalies.

Tetrachlorofluorescein Dibenzoate.—This compound cannot be prepared by the Baumann-Schotten reaction as shown under tetrachlorofluorescein monobenzoate but is readily made by the direct action of benzoyl chloride on the anhydrous tetrachlorofluorescein. Ten grams of anhydrous tetrachlorofluorescein were suspended in 100 cc. of benzoyl chloride and the mixture heated to the boiling point for one-half hour. At the end of this time the tetrachlorofluorescein was completely dissolved to a greenish brown liquid. When cold this solution was poured into 95% alcohol when the white dibenzoate separated out. This was filtered off and recrystallized from benzene, from which solvent it was obtained perfectly white. Melting point, 247°. When heated in a current of air to 130° this compound lost only 1.5% and no moisture condensed upon the cool part of the tube but the odor of benzene was noticeable. This compound, therefore, crystallizes without benzene of crystallization. A determination of chlorine on the product heated to constant weight at 130° shows that it is tetrachlorofluorescein dibenzoate.

Subst. 0.3025; cc. 0.1 N $AgNO_3$, 17.95.

Calculated for $C_{20}H_6Cl_4O_5(C_7H_5O)_2$, Cl, 21 20, found, 21 04.

Tetrachlorofluorescein dibenzoate is soluble in benzene, in acetone and in ethyl acetate, almost insoluble in alcohol. It is insoluble in aqueous solutions of the alkalies, and undergoes only slight hydrolysis when boiled with these solutions. It is slowly saponified by alcoholic solutions of the caustic alkalies.

Tetrachlorofluorescein Etherate.—The yellow hydrate dissolves completely in ether giving a light amber colored solution, and upon distilling off some of the ether an almost white compound, together with some of the dark red anhydrous tetrachlorofluorescein, crystallizes out. In order to obtain this white compound pure and free from the red, the following method was employed: Two grams of the air-dried yellow hydrate were dissolved in 200 cc. of anhydrous ether, the solution filtered from a very small amount of the red anhydrous tetrachlorofluorescein contained in the hydrate, and heated to boiling on a water bath in a flask fitted with a return condenser. The solution became lighter in color by this treatment, and upon cooling a few white crystals separated, together with some of the dark red anhydrous material. After filtering, some of the ether was distilled off below 20°, under reduced pressure, when white crystals separated. These were filtered off with the aid of suction but they turned yellow very quickly as the adherent ether evaporated, and became white again when moistened with ether or when brought into contact with ether vapor. In order to prevent this change to yellow the white crystals were filtered off on a Büchner funnel with suction, and while still moist with ether transferred quickly to a deep beaker and the remaining ether allowed to pass off slowly with a column of ether vapor above the crystals. By this means a perfectly white product was obtained. The change is probably due to a transformation of a part of the etherate to the yellow hydrate by the condensation of moisture upon the white crystals as the mechanically held ether rapidly evaporates. A weighed amount of the etherate was placed in a platinum boat and a rapid current of dry air at room temperature passed over it. At the end of twenty hours it was still losing weight and had become pale yellow in color. The substance was then gradually heated to 110° and came to constant weight at the end of seven hours. At no time did any moisture condense upon the cold part of the tube, and the material remained pale yellow in color. The tube was then heated to a temperature of 160° for fifteen minutes. Under this treatment the substance became pinkish yellow without any further loss in weight. The following results were obtained:

Subst. 0.4494, 0.2322; loss (ether) at 110°, 0.0607, 0.0308

Calculated for $C_{20}H_8Cl_4O_5.C_4H_{10}O$, 13.62; found, 13.51, 13.26

Determination I was made upon the air-dried, freshly prepared material, in II the substance had been kept in a stoppered bottle for four days.

Chlorine determinations on the material heated to constant weight at 110° gave the following results: Subst. 0.2504, 0.2012; cc. 0.1 *N* $AgNO_3$, 21.33, 17.03. Calculated for $C_{20}H_8Cl_4O_5$, Cl, 30.18; found, 30.21, 30.01.

Tetrachlorofluorescein etherate is a fairly stable, colorless, crystalline compound containing one molecule of ether. It loses this ether slowly in a current of dry air at room temperatures, more readily at 110°, leaving a pale yellow, anhydrous tetrachlorofluorescein in the lactoid form (see p. 710). When tetrachlorofluorescein etherate is heated with water it loses ether and the dark red (quinoid) anhydrous tetrachlorofluorescein is left. It is soluble in acetone and alcohol. Its solution in absolute alcohol gives tetrachlorofluoresceincarbinolcarboxylic acid when the alcohol is distilled off at 35°, under reduced pressure (see p. 690).

Compound of Tetrachlorofluorescein with Ethyl Acetate.—For the preparation of this compound five grams of the yellow hydrate were dissolved in 200 cc. of dry, freshly distilled ethyl acetate, the solution filtered to remove the small amount of red anhydrous tetrachlorofluorescein, and some of the solvent distilled off under reduced pressure. A white, beautifully crystalline compound separated out. This was treated in the same manner and with the same precautions as the etherate, when a perfectly white substance was obtained. This compound was placed in a tightly stoppered bottle and analyzed.

Subst. 0.4610, loss (ethyl acetate) at 130°, 0.1298.
Calculated for $C_{20}H_8Cl_4O_5.(CH_3COOC_2H_5)_2$, 27.26; found, 28.16.

When kept in a tightly stoppered bottle for two days:

Subst. 0.3034; loss, 0.0539.
Calculated for $C_{20}H_8Cl_4O_5.CH_3COOC_2H_5$, 15.78; found, 17.77

During the heating there was no condensation of moisture upon the cold part of the tube of the drying oven. The material remaining in the boat was pale yellow in color, and is the lactoid form of anhydrous tetrachlorofluorescein as shown by the following chlorine determination:

Subst. 0.2353, cc. 0.1 *N* $AgNO_3$, 19.97. Calculated for $C_{20}H_8Cl_4O_5$, Cl, 30.18; found, 30.10.

This compound with ethyl acetate resembles very closely in its properties and solubilities tetrachlorofluorescein etherate.

Monopotassium Salt.—For the preparation of this compound ten grams of the anhydrous tetrachlorofluorescein were suspended in 300 cc. of 95% alcohol and five grams of potassium acetate dissolved in 200 cc. of alcohol were added. The mixture was boiled in a flask fitted with a return condenser. At the end of half an hour the monopotassium salt crystallized out from the solution. This compound is light red in color and may be obtained beautifully crystallized from alcohol. The product thus obtained crystallizes with three molecules of water, as shown by the following analysis made on the air-dried material:

Subst. 0.1442; cc. 0.1 *N* $AgNO_3$, 10.33
Calculated for $C_{20}H_7Cl_4O_5K.3H_2O$, Cl, 25.24; found, 25.41

A potassium determination on the same material gave the following result: Subst. 0.2867; K_2SO_4, 0.0438. Calculated for $C_{20}H_7Cl_4O_5K.3H_2O$, K, 6.96; found, 6.87.

All of the water of crystallization is not removed from this salt by long heating to a temperature of 180°, one-half of a molecule remaining, as shown by the following determinations on the loss in weight:

Subst. 0.7925, 0.6270; loss (H_2O) at 180°, 0.0657, 0.0523
Calculated for $C_{20}H_7Cl_4O_5K.2.5H_2O$, 8.14; found, 8.29, 8.34

After heating to this temperature the salt was analyzed and gave the following results· Subst. 0.2664; cc. 0.1 *N* $AgNO_3$, 20.44. Calculated for $C_{20}H_7Cl_4O_5K.0.5H_2O$, Cl, 27.44; found 27.21.

A potassium determination on the same material gave the following result: Subst. 0.1511; K_2SO_4, 0.0252. Calculated for $C_{20}H_7Cl_4O_5K.0.5H_2O$, K, 7.56; found, 7.49

The monopotassium salt, therefore, contains three molecules of water of crystallization, and retains one-half a molecule on heating in dry air to a temperature of 180°. It is soluble in water and in methyl alcohol, difficultly soluble in ethyl alcohol.

Dipotassium Salt.—One hundred grams of the pure diacetate were suspended in one liter of absolute alcohol, and one liter of absolute alcohol containing 50 g. of potassium hydroxide was added. This mixture was boiled for an hour in a flask connected with a return condenser. Some of the alcohol was then distilled off and the potassium salt crystallized out. This salt was recrystallized from absolute alcohol several times, and the air-dried product gave the following results on analysis:

Subst. 0.2597, 0.2648; cc. 0.1 *N* $AgNO_3$, 16.36, 16.97; Calculated for $C_{20}H_6Cl_4O_5K_2.4.5H_2O$, Cl, 22.62; Calculated for $C_{20}H_6Cl_4O_5K_2.5H_2O$, Cl, 22.30, found, 22.35, 22.73

The determination of potassium by fuming down with concentrated sulfuric acid gave the following results: Subst. 0.2121, 0.3067; K_2SO_4, 0.0589, 0.0857; Calculated for $C_{20}H_6Cl_4O_5K_2.4.5H_2O$, K, 12.47; Calculated for $C_{20}H_6Cl_4O_5K_2.5H_2O$, K, 12.49; found, 12.46, 12.54

It was found to be impossible to remove all of the water of crystallization by heating without decomposing the salt—one molecule being held even when the salt was heated for a long time to a temperature of 170°. The analyses of the air-dried material indicate that it contains four and one-half or five molecules of water. It crystallizes from alcohol in beautiful dark red prisms having a cantharides green luster. These crystals are very soluble in water and in methyl alcohol, less soluble in ethyl alcohol, insoluble in ether and in acetone. Solutions of the dipotassium salt are red with a greenish fluorescence, if very dilute, yellowish red with a greenish fluorescence.

When a very dilute solution (0.5%) of the dipotassium salt is added to a slight excess of very dilute (tenth normal) acid, the yellow hydrate of tetrachlorofluorescein is precipitated. This precipitate becomes crystalline on boiling, with but little change in color. If, however, a stronger solution be added to a large excess of acid, and the mixture be boiled, the hydrate first formed is changed completely to the red anhydrous tetrachlorofluorescein.

Monosodium Salt.—This salt was prepared in the same manner as the monopotassium salt of tetrachlorofluorescein. Ten grams of the anhydrous tetrachlorofluorescein were suspended in 250 cc. of 95% alcohol, and five grams of anhydrous sodium acetate dissolved in 250 cc. of alcohol were added. After boiling for half an hour the monosodium salt separated out. This was filtered off, washed thoroughly with alcohol to remove any sodium acetate and analyzed.

Subst. 0.3927; loss (H_2O) at 150°, 0.0242.
Calculated for $C_{20}H_7Cl_4O_5Na.2H_2O$, 6.82; found, 6.16.

A sodium determination on the product dried at 150° gave the following result:

Subst. 0.1444; Na_2SO_4, 0.0206
Calculated for $C_{20}H_7Cl_4O_5Na$, Na, 4.68; found, 4.62

A chlorine determination on this salt dried at 150° gave the following result:

Subst. 0.1386; cc. 0.1 *N* $AgNO_3$, 11.31
Calculated for $C_{20}H_7Cl_4O_5Na$, Cl, 28.84; found, 28.94

The monosodium salt of tetrachlorofluorescein is orange-yellow in color, and is only slightly soluble in alcohol. When placed in water it undergoes hydrolysis and gives a colloidal solution of the yellow hydrate.

Disodium Salt.—This compound was prepared from the diacetate in a manner analogous to the preparation of the dipotassium salt, an alcoholic solution of sodium hydroxide being substituted for the alcoholic caustic potash. The disodium salt being much less soluble in absolute alcohol is precipitated out during the preparation—more completely when the solution is cooled. The salt was filtered off from the alcoholic solution and extracted with benzene to remove any unsaponified diacetate, and recrystallized from a mixture of methyl and ethyl alcohols, and then from absolute alcohol.

The following results were obtained on the material crystallized from absolute alcohol and dried in the air at room temperatures:

Subst. 0.2961, 0.3208; cc. 0.1 *N* $AgNO_3$, 19.53, 21.23
Calculated for $C_{20}H_6Cl_4O_5Na_2.5H_2O$, Cl, 23.49; found, 23.39, 23.47

The sodium determinations made by fuming down with concentrated sulfuric acid gave the following results: Subst. 0.1788, 0.2779; Na_2SO_4, 0.0416, 0.0652; Calculated for $C_{20}H_6Cl_4O_5Na_2.5H_2O$, Na, 7.57; found, 7.53, 7.60

This salt crystallizes from alcohol in dark red prisms very similar to the dipotassium salt—the dipotassium salt being a little darker in color. It is very soluble in water and soluble in methyl alcohol, but less soluble in ethyl alcohol than the dipotassium salt.

Action of Dry Ammonia on the Red Anhydrous Tetrachlorofluorescein.

Diammonium Salt of Tetrachlorofluorescein.—A weighed quantity of the red anhydrous tetrachlorofluorescein obtained by heating the yellow hydrate to constant weight at 110°, was placed in a platinum boat and a current of dry ammonia gas passed over it. The ammonia was dried by passing it through soda lime and then over sodium. The substance became darker in color, and absorbed ammonia very rapidly at first, but five days were required for the material to come to constant weight. The following results were obtained:

Subst. 0.5373, 0.6380; gain in wt., 0.0390, 0.0465; wt. of salt, 0.5763, 0.6845
Calculated for $C_{20}H_6Cl_4O_5(NH_4)_2$, NH_3, 6.76; found, 6.77, 6.79

When this diammonium salt is heated to 150° in a current of dry hydrogen it loses all of its ammonia and the original weight of the red anhydrous tetrachlorofluorescein is obtained.

Action of Dry Ammonia on the Colorless Anhydrous Tetrachlorofluorescein; Triammonia Salt of Tetrachlorofluorescein.—When the almost colorless lactoid form of tetrachlorofluorescein, obtained from the etherate or from the compound with ethyl acetate (see pp. 694 and 695), is placed in dry ammonia gas it turns bright red at once and there is an increase in weight corresponding to exactly *three* molecules of ammonia. If this salt be heated to a temperature of 110° in a current of dry air or hydrogen, all of the ammonia is lost and the almost colorless lactoid form of anhydrous tetrachlorofluorescein is obtained. This will again take up *three* molecules of ammonia. If this lactoid form be heated to a temperature of 160–170° for some time, it is converted without loss into the red anhydrous tetrachlorofluorescein, and will then absorb an equivalent of only *two* molecules of ammonia. The following results were obtained:

Subst. 0.1385, 0.4180; gain in wt., 0.0151, 0.0455, wt. of salt, 0.1536, 0.4635
Calculated for $C_{20}H_8Cl_4O_5(NH_3)_3$, NH_3, 9.81; found, 9.83, 9.82

The second determination was made on the lactoid form of the anhydrous tetrachlorofluorescein obtained from the compound with ethyl acetate (see p. 695).

When left exposed to the air this triammonia salt loses one molecule of ammonia very rapidly. The remainder of the ammonia is lost very slowly at room temperature, but very rapidly if heated to 110°.

Action of Dry Ammonia on Tetrachlorofluoresceincarbinolcarboxylic Acid.—When the carbinol carboxylic acid of tertachlorofluorescein is placed in dry ammonia it turns bright red at once and there is a considerable increase in volume. The increase in weight is very rapid at first, but at the end of one hour the substance begins to lose weight. The results taken at the point of greatest increase in weight show that the substance takes up an equivalent of *three* molecules of ammonia, with but little loss of water.

Subst. 0.4708, 0.3489; gain in wt., 0.0470, 0.0359; wt. of salt, 0.5178, 0.3848
Calculated for $C_{20}H_8Cl_4O_5(NH_3)_3.H_2O$, NH_3, 9.48, found, 9.08, 9.33.

When this ammonia salt is left in the ammonia there is a very gradual decrease in weight. Even after remaining in a slow current of dry ammonia for one week the material did not come to constant weight. When this salt is heated in a current of air to 120°, it loses both water and ammonia—the loss on the original material being the same as that obtained when the carbinol acid is heated to constant weight at 170°. When this substance, which is yellowish red in color, is placed in ammonia an equivalent of exactly *two* molecules is absorbed, as in the case of the red anhydrous tetrachlorofluorescein. This is shown by the following result:

Subst. 0.4460; gain in wt., 0.0324; wt. of salt, 0.4784
Calculated for $C_{20}H_6Cl_4O_5(NH_4)_2$, NH_3, 6.76; found, 6.77

Action of Dry Ammonia on Tetrachlorofluorescein Hydrate.—The yellow hydrate of tetrachlorofluorescein turns bright red at once when placed in dry ammonia, and absorbs an equivalent of *three* molecules of ammonia with very little loss of water, as shown by the following determination:

Subst. 0.4940; gain in wt., 0.0541; wt. of salt, 0.5481
Calculated for $C_{20}H_8Cl_4O_5(NH_3)_3.H_2O$, NH_3, 9.48; found, 9.87

When this salt is heated in a current of air to a temperature of 150°, both ammonia and water are given off and the red anhydrous tetrachlorofluorescein is obtained. The weight of this material is less than the weight of the yellow hydrate used at the beginning of the determination, and the loss is equivalent to nearly one molecule of water, as shown by the following:

Yellow hydrate, 0.4940; red anhydrous product, 0.4786; loss, 0.0154
Calculated for $C_{20}H_8Cl_4O_5.H_2O$, H_2O, 3.69; found, 3.12

Tetrachlorofluorescein Methyl Ester.—This compound was prepared in the following manner: Ten grams of pure anhydrous tetrachlorofluorescein were suspended in 500 cc. of methyl alcohol and 100 grams of concentrated sulfuric acid added. This mixture was boiled on the water bath for one hour when the tetrachlorofluorescein had completely dissolved. About one-half of the methyl alcohol was then distilled off and the remaining solution poured into water when the dark red methyl ester was precipitated. This was filtered off, washed thoroughly with water to remove sulfuric acid, dried, and recrystallized from benzene. The product thus obtained crystallizes without benzene of crystallization since the loss in weight is inconsiderable—being less than 1%—when the air-dried material is heated in a current of air to 150°.

A chlorine determination on the material dried to constant weight at 150° resulted as follows:

Subst. 0.1545; cc. 0.1 *N* $AgNO_3$, 12.64
Calculated for $C_{20}H_7Cl_4O_5CH_3$, Cl, 29.12; found, 29.00

The monomethyl ester of tetrachlorofluorescein is insoluble in water, difficultly soluble in methyl alcohol, soluble in ethyl alcohol, and very soluble in acetone and in benzene. It dissolves in cold aqueous solution of caustic soda and is precipitated out again unchanged upon the addition of acids. It is insoluble in *cold* aqueous solutions of the alkaline carbonates, but dissolves slowly when the solution is boiled, and separates out on cooling. The alkaline solutions of the methyl ester have the same color and fluorescence as the alkaline solutions of tetrachlorofluorescein itself. Strong hot hydrochloric acid (sp. gr. 1.10) dissolves the methyl ester with difficulty, forming the orange hydrochloride which crystallizes out on cooling.

Tetrachlorofluorescein methyl ester does not absorb ammonia even when kept in a current of dry ammonia for several days.

Action of Dry Hydrochloric Acid Gas on Tetrachlorofluorescein Methyl Ester. Tetrachlorofluorescein Methyl Ester Hydrochloride.—When the dark red methyl ester is placed in a current of dry hydrochloric acid gas, it becomes orange in color and absorbs an equivalent of nearly two molecules of hydrochloric acid, as shown by the following:

Subst 0.1958; hydrochloride, 0.2219
Calculated for $C_{20}H_7Cl_4O_5CH_3$ 2HCl, HCl, 13.14; found, 11.76

When this compound is placed in a current of dry air at room temperatures, the excess of hydrochloric acid above one molecule is lost very readily, and the hydrochloride of tetrachlorofluorescein methyl ester is obtained, as shown by the following:

Subst. 0.1958, hydrochloride, 0.2104
Calculated for $C_{20}H_7Cl_4O_5CH_3$ HCl, HCl, 7.04, found, 6.94

Action of Dry Hydrochloric Acid Gas on Fluorescein; Fluorescein Hydrochloride.—A weighed quantity of the dark red anhydrous fluorescein, obtained by saponification of the pure diacetate of fluorescein, was placed in a platinum boat and subjected to the action of dry hydrochloric acid gas. The material became light yellow in color and absorbed an equivalent of one molecule of hydrochloric acid. This yellow substance is fluorescein hydrochloride as shown by the following result:

Subst 0.2724; hydrochloride, 0.3058
Calculated for $C_{20}H_{12}O_5$ HCl, HCl, 10.98; found, 10.92

When heated in a current of air to a temperature of 150° this hydrochloride loses all of its hydrochloric acid and the original weight of dark red fluorescein remains.

The light yellow hydrochloride of fluorescein is also formed when the dark red fluorescein is boiled in concentrated hydrochloric acid.[1] It is slightly soluble in the hydrochloric acid with a yellow color but without fluorescence.

Dry hydrochloric acid gas is not absorbed by the red anhydrous or the colorless anhydrous tetrachlorofluorescein. When the red anhydrous tetrachlorofluorescein is boiled with concentrated hydrochloric acid no color is imparted to the solution nor is there any noticeable change in the tetrachlorofluorescein.

Tetrachloroeosin.—The bromination of tetrachlorofluorescein was carried out in the following manner: Ten grams of pure anhydrous tetrachlorofluorescein were suspended in forty grams of glacial acetic acid and 75 grams of a 20% solution of bromine in glacial acetic acid were added. The greater part of the tetrachlorofluorescein dissolved at first, but at the end of five minutes the tetrachloroeosin began to crystallize out. The mixture was allowed to stand over night, then heated on a water bath for ten or fifteen minutes and allowed to cool. The crystals which separated were filtered off and washed with glacial acetic acid. Yield, ten grams. This substance, which was dirty pink in color, was dissolved in glacial acetic acid and the solution filtered while hot. Upon cooling this solution, white crystals of tetrachloroeosin separated. The material thus obtained was filtered off with suction and washed with glacial acetic acid.

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[1] Compare Gattermann, *Ber.*, 32, 1135 (1899).

When washed with water or alcohol these white crystals of tetrachloroeosin became pink. This color was removed by washing again with glacial acetic acid. The compound was exposed in the air until it no longer had the odor of acetic acid and was then analyzed.

Subst. 0.4582, 0.6231; loss (acetic acid) at 150°, 0.0339, 0.0453.
Calculated for $C_{20}H_4Cl_4Br_4O_5.CH_3COOH$, 7.08; found, 7.40, 7.27.

The air-dried product crystallized from glacial acetic acid loses one molecule of acetic acid when heated to a temperature of 150°, and no water condensed on the cold part of the tube. The compound remains white unless it is heated above 150° or the heating be continued for a long time at 150°, when it becomes light pink in color.

The chlorine and bromine determinations on tetrachloroeosin and its derivatives were made in the following manner: A weighed quantity of the material was mixed with lime, placed in a Jena glass tube and heated in the same manner as in the determination of chlorine.[1] After heating the contents of the tube were dissolved in dilute nitric acid, the carbon filtered off and thoroughly washed with water. A measured excess of tenth-normal silver nitrate was then added to the filtrate and the mixture of silver halides filtered off on a weighed Gooch crucible. After washing thoroughly with 1% nitric acid, the mixture of silver halides on the Gooch was dried to constant weight at 145°, and the weight recorded. The excess of silver nitrate in the filtrate was then titrated with tenth-normal ammonium thiocyanate solution. From the weight of the silver halides and the volume of the tenth-normal silver nitrate solution required to precipitate them, the percentage of chlorine and bromine in the original compound can be indirectly determined, using the following formulas:[2]

$$\text{Percentage of chlorine} = C - 53.249B/0.6676\,A$$
$$\text{Percentage of bromine} = 69.763\,B - C/0.38809\,A$$

in which A = the weight of the substance taken
B = the weight of the silver halides
C = the volume in cc. of the tenth-normal silver nitrate solution required to exactly precipitate the chloride and bromide.

As a check upon this indirect method of determination, the mixture of silver chloride and bromide on the Gooch was treated with dry chlorine gas until there was no further loss in weight. The silver bromide was thus completely converted into silver chloride. The percentage of the two halides in the original substance can be calculated from this loss in weight and the weight of the silver halides, by means of the following formulas:

$$\text{Percentage of chlorine} = 24.739\,B - 104.495\,D/A$$
$$\text{Percentage of bromine} = 179.76\,D/A$$

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[1] *Am. Chem. J.*, 41, 393 (1909).

[2] *Ibid.*, 41, 380 (1909).

in which A = the weight of the substance taken
B = the weight of the silver halides
D = the decrease in weight of the silver halides on treatment with chlorine

Halogen determinations on tetrachloroeosin crystallized from glacial acetic acid and heated to constant weight at 150°, gave the following results:

	Substance. Gram.	Silver halides. Gram.	Tenth-normal silver nitrate. Cc.	Chlorine. Per cent.	Bromine. Per cent.
I.................	0.1994	0.3286	19.88	17.90	39.41
II.................	0.2109	0.3478	21.02	17.76	39.63
III.................	0.2324	0.3801	22.96	17.53	39.47
IV.................	0.1896	0.3147	19.02	17.86	39.96

In Determinations III and IV the mixture of silver halides was treated with chlorine and the following results obtained:

Substance. Gram.	Silver halides. Gram.	Decrease. Gram.	Chlorine. Per cent.	Bromine. Per cent.
0.2324	0.3801	0.0506	17.71	39.14
0.1896	0.3147	0.0430	17.36	40.77
Calculated for $C_{20}H_4Cl_4Br_4O_5$ ...		....	18.06	40.69
Calculated for $C_{20}H_4Cl_4Br_4O_5\,H_2O$..		. . . .	17.65	39.78

These results seem to show that the substance is tetrachloroeosin with one molecule of water, that is, that it may be the carbinol-carboxylic acid of tetrachloroeosin. It will be seen that the percentages of chlorine and bromine in the two compounds are so close together as to be within the limit of experimental error. Especially is this the case, since an error of 0.01 cc. in reading the volume of the silver nitrate solution makes a difference of 0.10% in the percentage of bromine, and an error of 0.0001 g. in the weight of silver halides makes a difference of 0.20%. It is therefore impossible to state with certainty, from the results of the halogen determinations alone, whether the compound is anhydrous tetrachloroeosin or tetrachloroeosincarbinolcarboxylic acid.

If this substance does contain a molecule of water it does not lose this water when heated for twenty-four hours at a temperature of 190–200° in a current of dry air, but becomes pink without any loss in weight. In this respect it is analogous to the lactoid form of tetrachlorofluorescein (see pp. 695 and 696). One gram of this white material was dissolved in nitrobenzene, which had been previously heated to boiling for some time to remove all the water. The dark red solution was then boiled in a distillation flask, but no moisture collected upon the cold neck of the flask. From these facts, and from the behavior of the compound when placed in dry ammonia (see p. 706), it seems highly probable that the substance is the anhydrous tetrachloroeosin.

This tetrachloroeosin dissolves in alcohol, acetone, ether, ethyl acetate, chloroform, benzene, nitrobenzene and carbon disulfide. It is difficultly soluble in glacial acetic acid. The alcohol and acetone solutions are reddish pink in color with a greenish yellow fluorescence, while the solution in ether is pink without any fluorescence. The color of these solutions is destroyed by the addition of a drop of mineral acid. The solutions in ethyl acetate, chloroform, benzene, and carbon disulfide are colorless. The solution in nitrobenzene is dark red in color and probably contains the quinoid modification. Dilute solutions of the alkalies and alkaline carbonates dissolve tetrachloroeosin with a cherry-red color and greenish fluorescence. In very dilute alcoholic solutions of the alkalies the fluorescence is brick-red (see p. 709). If strong alkali be added in large excess the color becomes purple, then blue, *without any fluorescence*. If this solution be diluted at once, it becomes red with a greenish fluorescence. The same color change is observed if an insufficient amount of acid be added at once to this strong alkaline solution. If the strong alkaline solution be allowed to stand over night, and the greenish blue solution is then diluted with water, a deep blue solution without fluorescence results, like that obtained when gallein or tetrachlorogallein is dissolved in an excess of dilute alkali. If this blue solution be heated to boiling it becomes red, with the characteristic greenish fluorescence of tetrachloroeosin in dilute alkali. When the greenish blue strong alkaline solution is poured into an excess of acid a pink precipitate forms which dissolves in dilute alkali with a *blue* color without fluorescence. This blue solution changes to red with a greenish fluorescence, when heated or on long standing. This change in strong alkaline solution is probably due to the formation of a tetrapotassium salt of tetrachloroeosin (see p. 722).

Tetrachloroeosin Hydrate.—This compound was prepared in a manner analogous to the preparation of tetrachlorofluorescein hydrate (see p. 688). Five grams of the anhydrous tetrachloroeosin were dissolved in 500 cc. of water containing two grams of potassium hydroxide. This solution was filtered, diluted to two liters and poured, with constant stirring, into water containing an excess of hydrochloric acid. The reddish pink precipitate thus obtained was washed throughly by decantation, filtered on a Buchner funnel and washed free from chlorides. The product on drying in the air becomes lighter in color and loses some of its combined water, as shown by the following results on analysis:

Subst. 0.6424, 0.5428; loss (H_2O) at 110°, 0.0079, 0 0065
Calculated for $C_{20}H_4Cl_4Br_4O_5.H_2O$, 2 24, found, 1.23, 1.20

When heated to constant weight at 110° the pink hydrate loses water very readily and becomes almost white. This faintly pink compound is anhydrous tetrachloroeosin, as shown by the following halogen determinations:

	Substance. Gram.	Silver halides. Gram.	Tenth-normal silver nitrate. Cc.	Chlorine. Per cent.	Bromine. Per cent.
I..................	0.1767	0.2930	17.73	18.01	39.60
II..................	0.2144	0.3584	21.65	17.96	40.25
			Decrease. Gram.		
II.............. .	0 2144	0.3584	0.0481	17 91	40 32
Calculated for $C_{20}H_4Cl_4Br_4O_6$..				18 06	40.69

Tetrachloroeosin hydrate is soluble in alcohol, acetone, ether, and ethyl acetate, difficultly soluble in chloroform, and in benzene. When treated with solutions of the alkalies or alkaline carbonates, it behaves in the same manner as the anhydrous tetrachloroeosin (see p. 704). When treated with glacial acetic acid at ordinary temperatures, or more readily on heating, it turns white, forming the compound of tetrachloroeosin with glacial acetic acid described above (see p. 702). The hydrate is insoluble in petroleum ether and in ligroin. When boiled with these solvents it becomes white, probably being transformed into the anhydrous tetrachloroeosin.

Tetrachloroeosin Diacetate.—Five grams of pure anhydrous tetrachloroeosin were mixed with five grams of anhydrous sodium acetate and 50 g. of acetic anhydride. This mixture was boiled for four hours, and, upon cooling, almost white crystals of the diacetate separated. This material was filtered off, washed thoroughly with water, and extracted with absolute alcohol to remove any unacetylated tetrachloroeosin. When this residue was crystallized from acetone a perfectly white compound was obtained, which did not contain any acetone and melted at 298° to 300°. This product was then recrystallized from ethyl acetate and heated to 150° until all the ethyl acetate of crystallization was removed. The melting point remained unchanged. The perfectly white diacetate obtained from the ethyl acetate solution, and dried in the air, gave the following results on analysis:

Subst. 1.1649; loss (ethyl acetate) at 150°, 0.1035
Calculated for $C_{20}H_2Cl_4Br_4O_5(COCH_3)_2\ CH_3COOC_2H_5$, 9.20; found, 8.88

No moisture collected upon the cold part of the tube of the electric oven, but the odor of ethyl acetate was very noticeable. The compound therefore loses some of its ethyl acetate on drying in the air.

A halogen determination on the substance heated to 150° gave the following result:

Subst. 0.1926; silver halides, 0.2915; cc. 0.1 *N* $AgNO_3$, 17.63
Calculated for $C_{20}H_2Cl_4Br_4O_5(COCH_3)_2$, Cl, 16.31; Br, 36.76; found, 16.37, 36.30

Tetrachloroeosin diacetate is soluble in acetic anhydride, benzene, acetone, ethyl acetate, and but slightly soluble in alcohol. When treated with alcoholic solutions of the alkalies it undergoes saponification even in the cold, quite readily when heated to boiling. Aqueous solutions of the alkalies hydrolyze this diacetate but slightly. It dissolves in concentrated sulfuric acid with a pink color and greenish fluorescence, probably undergoing hydrolysis, for when this solution is diluted with water a pink compound, the hydrate, is precipitated.

Dipotassium Salt of Tetrachloroeosin.—Five grams of anhydrous tetrachloroeosin were dissolved in 200 cc. of alcohol and 100 cc. of a solution of alcoholic caustic potash, containing three grams of potassium hydroxide, were added. This red solution was heated to boiling for half an hour, then some of the solvent was distilled off. Dark red crystals of the dipotassium salt separated. These were washed thoroughly with alcohol, dried to constant weight at 150° and analyzed. A determination of potassium showed that this substance was not pure, but contained some of the tetrapotassium salt. (See p. 704.) The material was then recrystallized twice from alcohol, dried in the air, and analyzed. The following results were obtained:

Subst. 1.1689; loss (H_2O) at 150°, 0 1009; Calculated for $C_{20}H_2Cl_4Br_4O_5K_4.4\ 5H_2O$, 8.60; Calculated for $C_{20}H_2Cl_4Br_4O_5K_2.5H_2O$, 9.46; found, 8.83

A determination of potassium in the salt dried to constant weight at 150° gave the following result:

Subst. 0.1248; K_2SO_4, 0.0254; Calculated for $C_{20}H_2Cl_4Br_4O_5K_2$, K, 9 07; found, 9.13

Attempts to prepare the monosodium salt of tetrachloroeosin in a manner similar to the preparation of the monosodium salt of tetrachlorofluorescein, *i. e.*, by the action of anhydrous sodium acetate upon the anhydrous tetrachloroeosin in alcoholic solution, resulted in the formation of a mixture of the mono- and disodium salts. These two salts could not be separated by repeated crystallization from alcohol.

Action of Dry Ammonia on Tetrachloroeosin.—When the white compound, obtained by heating the tetrachloroeosin crystallized from glacial acetic acid (see p. 702) to constant weight at 150°, is placed in a current of dry ammonia it turns red at once, and absorbs ammonia very rapidly with a large increase in volume and evolution of heat. The following result was obtained:

Subst. 0.2256; gain in wt., 0.0237; wt. of salt, 0.2493
Calculated for $C_{20}H_4Cl_4Br_4O_5.5NH_3$, NH_3, 9.78; found, 9.51.

When the red ammonium salt thus formed is heated in a current of air to a temperature of 150°, all of the ammonia is lost and the original weight of white material is obtained. During this heating, no moisture collected upon the cold part of the tube, the loss in weight being due entirely to loss of ammonia. In the case of the compound formed by the action of ammonia on tetrachlorofluoresceincarbinolcarboxylic acid (see p. 699), however, both ammonia and water are given off, and hence the white substance obtained by heating the compound crystallized from glacial acetic acid to constant weight at 150°, must be the lactoid form of tetrachloroeosin and not the colorless carbinol carboxylic acid (see p. 721).

When the light pink tetrachloroeosin obtained by heating the pink hydrate to constant weight at 110° is placed in dry ammonia it behaves in the same manner as the white tetrachloroeosin described above. This is shown by the following result:

Subst. 0.5363; gain in wt., 0 0561, wt of salt, 0.5924

Calculated for $C_{20}H_4Cl_4Br_4O_5.5NH_3$, NH_3, 9 78; found, 9.47

When this red salt is heated in a current of air to a temperature of 150°, all the ammonia is lost, no moisture collected upon the cold part of the tube, and the original weight of the light pink tetrachloroeosin was obtained.

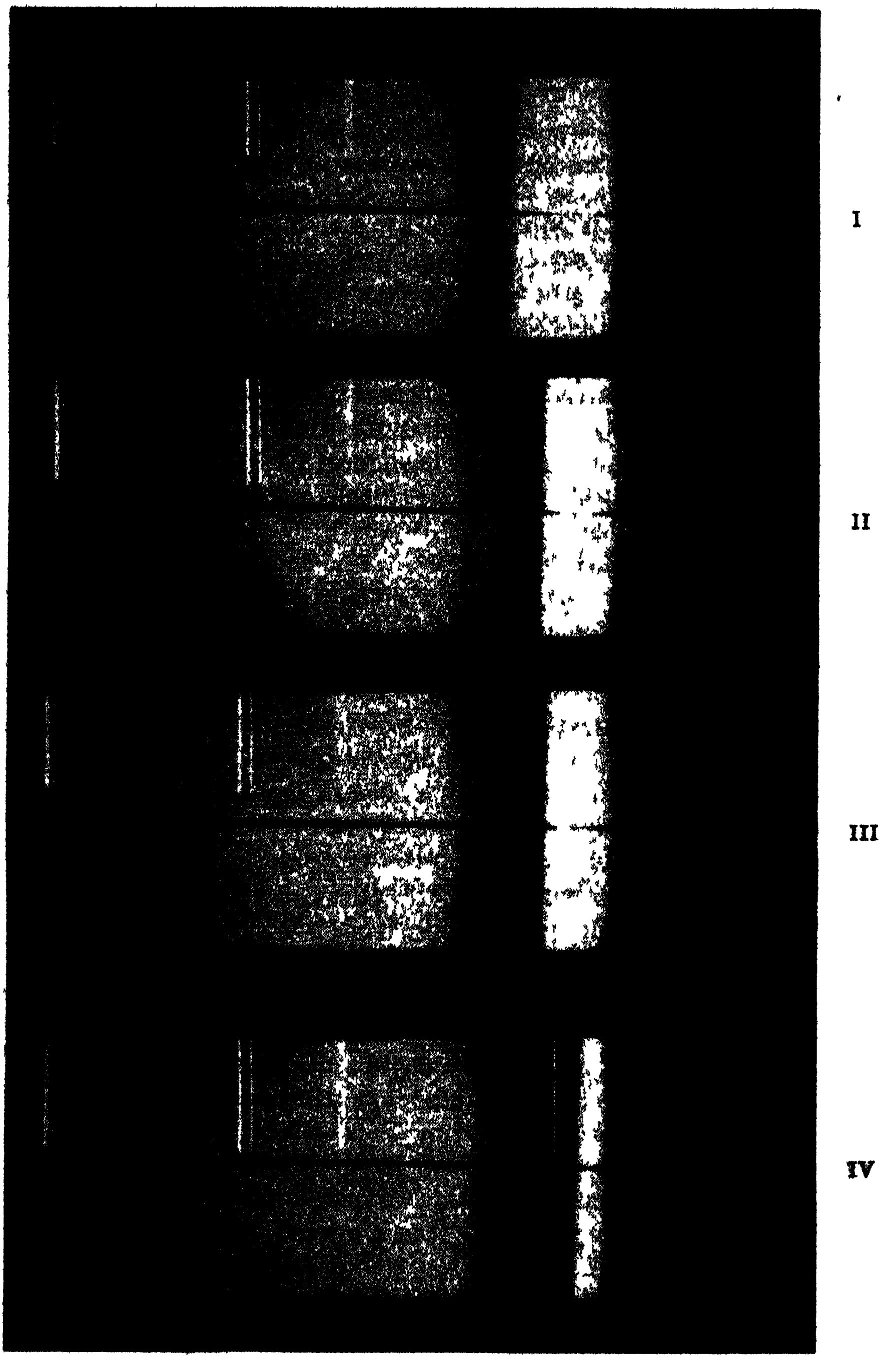
Absorption and Fluorescence Spectra of Solutions of Fluorescein, Tetrachlorofluorescein, Eosin and Tetrachloroeosin.

Professors E. L. Nichols and Ernest Merritt have examined solutions of fluorescein, tetrachlorofluorescein, eosin and tetrachloroeosin, and have furnished the following description of the absorption and fluorescence spectra of these solutions:

"Photographs of the absorption spectra of fluorescein (I), tetrachlorofluorescein (II), eosin (III), and tetrachloroeosin (IV), were made with different thicknesses of solution ranging from 2 mm. to 15 mm. The solutions were prepared as follows: The phthalein was suspended in neutral absolute alcohol and an amount of alcoholic caustic potash equivalent to four molecules of the alkali to one of the phthalein was added. The solutions were then diluted with neutral absolute alcohol until the absorption bands could be clearly seen through a layer of liquid 10 mm. thick. The following concentrations were used: Fluorescein, 4.37 mg. per liter; tetrachlorofluorescein, 12.42 mg. per liter; eosin, 19.25 mg. per liter; tetrachloroeosin, 26.00 mg. per liter.

"As a source of light the acetylene flame was used in all cases. For showing the general character of the absorption spectrum a thickness of approximately 10 mm. was found to be best and this was the thickness used in making the photographs here reproduced.

"It will be noticed that with the concentration and thickness used the absorption of fluorescein is less marked than that of either of the other substances. The chief band lies in the blue with its crest approximately at 0.501 μ. There is a second fainter band, which does not show on the photograph, lying toward the red and having its crest approximately at 0.528 μ. The bands are so broad that the crests cannot be located with accuracy and the wave lengths given are approximations only. The absorption of tetrachlorofluorescein is more marked and is very nearly identical with that of eosin. In each case two bands are clearly seen, the denser one lying toward the red. The crests of these bands are approximately


I
II
III
IV

0.523μ and 0.501μ for the tetrachlorofluorescein, and 0.523μ and 0.490μ for the eosin.

"The absorption bands of tetrachloroeosin are sharper than with any of the other substances. The two bands which appear in the photograph have their crests at approximately 0.553μ and 0.510μ.

"Upon some of the negatives taken there was evidence that the more intense band in the case of tetrachlorofluorescein, eosin, and tetrachloroeosin was in each case double; but we have found it impossible to obtain negatives in which the division is sufficiently sharp to show in the reproduction. The wave lengths given for the denser bands of these three substances are therefore to be regarded as the average for the two bands that are in all likelihood present.

"Perhaps the most striking point that is noticed in comparing the absorption spectra of the four substances is the increasing wave length of the absorption bands as we pass from fluorescein to tetrachloroeosin in the order shown in the photograph. The wave length of the absorption bands increases constantly with the number of the halogen atoms introduced into the molecules of fluorescein.

"A few preliminary tests at the temperature of liquid air indicate that the absorption at that temperature is considerably increased and that the existence of three bands in the absorption spectrum of tetrachloroeosin is more readily demonstrated at that temperature than at ordinary temperatures. There is no evidence, however, that the absorption bands become extremely narrow as is the case in some fluorescent substances, for example, the uranyl compounds.

"All of the substances show strong fluorescence, the color changing from greenish yellow with fluorescein to brick-red with tetrachloroeosin. This change is to be expected, since in fluorescent substances of this type the fluorescence band always lies immediately toward the red from the absorption bands.

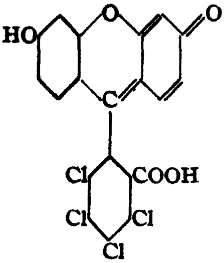
"The crests of the fluorescence bands are at approximately the following wave lengths:

Fluorescein	0.530μ
Tetrachlorofluorescein	0.554μ
Eosin	0.558μ
Tetrachloroeosin	0.585μ

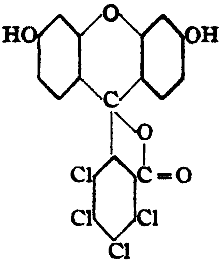
"There is some indication that the fluorescence bands are complex—as is to be expected on account of the complexity of the absorption spectrum—but a careful spectrophotometric study of the spectra would be required to establish this fact."

Theoretical.

The results of this investigation show that tetrachlorofluorescein exists in two forms. One is dark red and the other, colorless. The dark red modification is the more stable of the two. It is obtained by heating the yellow hydrate to constant weight at 110°, and from tetrachlorofluoresceincarbinolcarboxylic acid and the acetonate of tetrachlorofluorescein by heating to a temperature of 150–160°. The colorless form of tetrachlorofluorescein may be obtained from the etherate and also from the compound with ethyl acetate, by heating in a current of *dry* air to 110°. This colorless modification goes over without loss of weight to the dark red form on heating for some time to 150–160°. Because of its color, the quinoid formula I is assigned to the dark red tetrachlorofluorescein, while the lactoid formula II best represents the colorless modification.



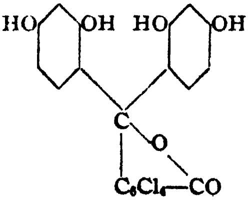
I. Tetrachlorofluorescein (colored).



II. Tetrachlorofluorescein (colorless).

As derivatives of the quinoid formula (I) there have been prepared tetrachlorofluorescein hydrate (yellow), tetrachlorofluorescein methyl ester (dark red), the dipotassium, disodium and diammonium salts (dark red), the monopotassium salt (light red), and the monosodium salt (orange). The following colorless compounds must be regarded as derived from the lactoid Formula (II): The diacetate, dibenzoate and monobenzoate of tetrachlorofluorescein, the acetate of the monobenzoate, tetrachlorofluorescein etherate, and the compound of tetrachlorofluorescein with ethyl acetate. Another colorless modification of tetrachlorofluorescein, the carbinol carboxylic acid (see p. 690), has also been prepared. The colorless acetonate described on p. 689 is probably a mixture of this carbinol acid and the diacetonate (see p. 714).

To the yellow hydrate, obtained by precipitating the caustic alkaline solution of tetrachlorofluorescein with acid, Graebe[1] assigns the lactoid formula



Tetrachlorofluorescein hydrate, according to Graebe.

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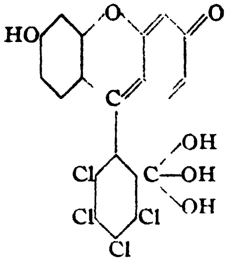
[1] *Ann. der Chemie*, 238, 334 (1887).

Since this compound is *colored*, and loses its molecule of water *very readily* (see p. 688), it probably has the *quinoid* structure. It must therefore be represented by the following formula:



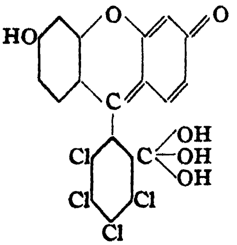
Tetrachlorofluorescein hydrate.

This is in accord with the fact that the hydrate acts like a strong acid, decomposing the alkaline carbonates and acetates with the formation of salts, and reacting with methyl alcohol to form an ester.

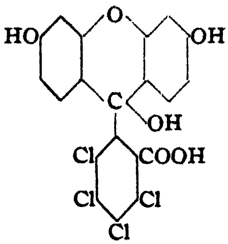
This hydrate is also formed, contrary to the statement of Graebe, when a dilute ammonia or sodium carbonate solution of tetrachlorofluorescein is precipitated in the cold by acid (see p. 689). When any dilute alkaline solution of tetrachlorofluorescein is precipitated *at the boiling temperature* by acid, a mixture of the yellow hydrate and the red anhydrous compound results. This is also contrary to Graebe's statement.

The above structure for the hydrate is confirmed by the fact that on treatment with acetic anhydride it yields the same diacetate as the anhydrous tetrachlorofluorescein, and not a *tetracetate*, as might be expected if this compound has the structure assigned to it by Graebe. The yellow hydrate loses water very slowly when left exposed to the air at room temperature, more readily in a vacuum desiccator over phosphorus pentoxide, and very rapidly when heated to 110°. This is contrary to the result obtained by Graebe, who states that tetrachlorofluorescein hydrate (tetrachloro-orthofluorescein) loses no weight at 110°, and undergoes but little change at 150–160°. From these results it seems probable that Graebe's tetrachloro-orthofluorescein was analyzed after crystallization of the precipitated hydrate from alcohol. If such was the case, it was a mixture of tetrachlorofluoresceincarbinolcarboxylic acid and a little of the hydrate, since it has been shown that the yellow hydrate when crystallized from alcohol is almost completely converted into the carbinol acid (see p. 690). This carbinol acid loses water only *very* slowly at 110°, and slowly at 150–160°. Such an explanation would account for the results obtained by Graebe. It is interesting to note that this yellow hydrate yields the colorless lactoid form of tetrachlorofluorescein when dehydrated at ordinary temperatures over phosphorus pentoxide, while at 110° it gives the deep red modification.

When prepared from the yellow hydrate as described on p. 690 the carbinol acid is colorless. This change must be accompanied by a molecular rearrangement and may be represented as follows:



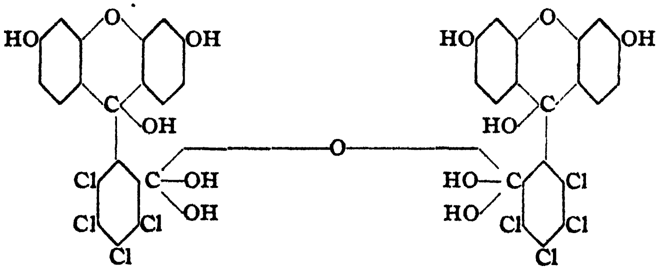
Tetrachlorofluorescein hydrate (colored).



Tetrachlorofluoresceincarbinol-carboxylic acid (colorless).

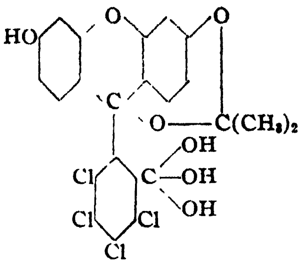
When this carbinol acid is dissolved in sodium hydroxide, the sodium salt of tetrachlorofluorescein is formed, and when the solution is acidified the yellow hydrate is precipitated. It is thus possible to reverse the above process, and convert the carbinol acid back into the yellow hydrate. When heated to 180° for an hour it is converted entirely into the dark red anhydrous tetrachlorofluorescein, and this change also takes place when the substance is boiled for some time with water.

From the fact that the carbinol acid loses almost exactly one and one-half molecules of water when heated to 180°, and loses no weight when kept for a long time in an evacuated desiccator over phosphorus pentoxide, it must be represented by the formula $C_{20}H_{10}Cl_4O_6 + 0.5H_2O$. The acid, therefore, crystallizes with half a molecule of water, and the structural formula is probably



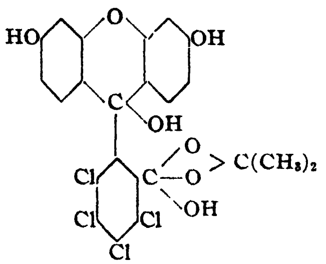
Tetrachlorofluoresceincarbinolcarboxylic acid.

When the hydrate is dissolved in dry acetone and some of the solvent distilled off, a white compound separates. This substance contains both acetone and water, but the percentage of acetone is less than and the percentage of loss greater than that calculated for either of the two possible chemical individuals containing both water and acetone—an acetonate of the hydrate (Formula I) or an acetonate of the carbinol acid (Formula II).



Acetonate of the hydrate.

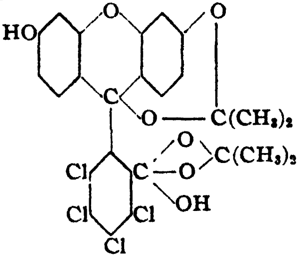
(I)



Acetonate of the carbinol acid.

(II)

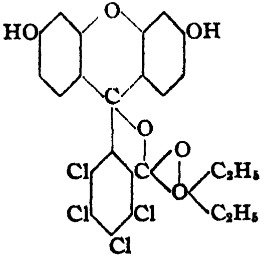
It therefore seems probable that this white substance is a mixture of the diacetonate[1] of tetrachlorofluorescein (Formula III) and the hydrate, or a mixture of the diacetonate and the carbinol acid. The fact that this substance is so nearly white, and that it has to be heated for a long time at 150° before it ceases to lose weight, leads to the belief that it is a mixture of the diacetonate and the carbinol acid. It will be remembered that the carbinol acid is obtained from the alcoholic solution of the yellow hydrate in a similar manner (see p. 690).



Tetrachlorofluorescein diacetonate.

(III)

When the yellow hydrate is dissolved in dry ether, and the excess of the solvent distilled off below 20°, under reduced pressure, the white tetrachlorofluorescein etherate crystallizes out. Since this compound is colorless and loses all of its ether readily at 100°, to give the colorless anhydrous tetrachlorofluorescein, it probably has the lactoid structure and may be represented by the following formula:



Tetrachlorofluorescein etherate (colorless).

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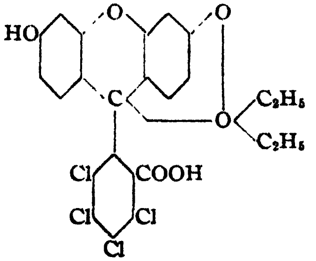
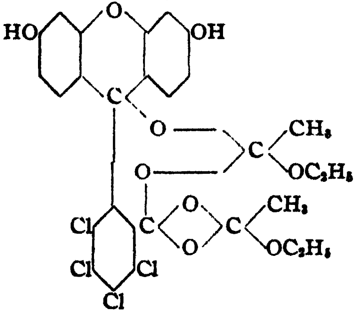
[1] *Am. Chem. J.*, 46, 13 (1911).

That the ether is attached to the carbonyl group of the phthalic acid residue and not to the quinoid grouping seems very likely since the compound loses no water, although made from the hydrate, and since, on treatment with water, the yellow hydrate results. This assumption seems all the more probable since the colorless etherate loses all of its ether in a current of *dry* air *at room temperatures*, and the *colorless* anhydrous tetrachlorofluorescein remains. If this compound had the structure,



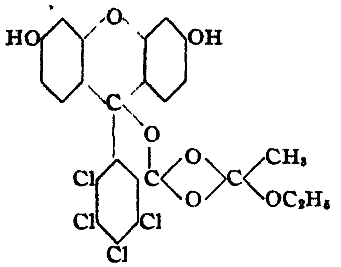
the dark red anhydrous tetrachlorofluorescein would probably result upon the loss of ether.

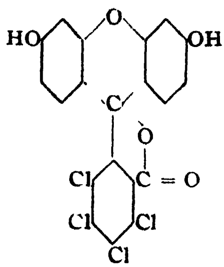
The compound of tetrachlorofluorescein with ethyl acetate, which is made in a manner similar to the preparation of the etherate, is also colorless. When first prepared the dry substance contains two molecules of ethyl acetate, and no water. When this compound is allowed to stand for some time in a stoppered bottle, one molecule of ethyl acetate is lost. The remaining molecule of ethyl acetate is driven off when the compound is heated in a current of dry air to a temperature of 130°, and the lactoid form of anhydrous tetrachlorofluorescein results. At no time during the loss of ethyl acetate does the substance become colored. In order to account for these facts the following structural formula is suggested:



Compound of tetrachlorofluorescein with ethyl acetate.

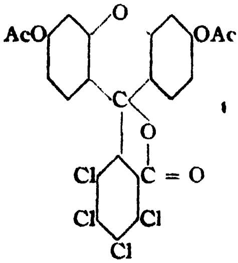
Both the ethyl acetate molecules are represented as attached to the phthalic acid residue, because of the fact stated above, that the compound loses one molecule of ethyl acetate very readily and does not become colored. The products formed by the loss of ethyl acetate may be represented by the following structural formulas:





A different condition obtains in the case of the diacetonate of tetrachlorogallein[1] where one of the acetone molecules is represented as attached to the quinoid grouping. This structure is given the compound because of the fact that a *colored* monacetonate is formed by the loss of one molecule of acetone.

That tetrachlorofluorescein contains two phenolic hydroxyl groups is shown by the fact that it forms a colorless diacetate and a colorless dibenzoate. Since both of these compounds are white and are insoluble in alkalies, they probably have the lactoid structure and may be represented by the formula in which Ac represents an acetyl or a benzoyl group:



Tetrachlorofluorescein diacetate and dibenzoate.

The colorless monobenzoate of tetrachlorofluorescein dissolves in dilute solutions of the alkalies and alkaline carbonates with a yellow color and a greenish fluorescence. When the colorless monobenzoate is heated to a temperature of 150° for some time it becomes yellow without loss of weight. This change in color is probably accompanied by a change of structure. The colorless compound is therefore represented by the lactoid Formula I, while the colored modification and its sodium salt must have the quinoid structure as shown by Formula II.

It is interesting to note that while fluorescein gives a *di*benzoate by the Baumann-Schotten reaction, tetrachlorofluorescein gives only a *mono*benzoate. This is another indication of the fact that tetrachlorofluorescein is more acid than fluorescein (see p. 719).

The acetate of the monobenzoate (see p. 693) also shows the presence

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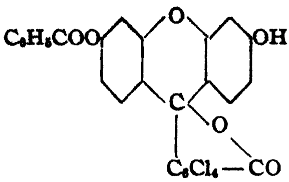
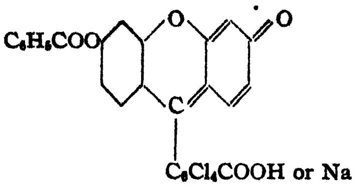
[1] *Am Chem. J*, 46, 10 (1911).



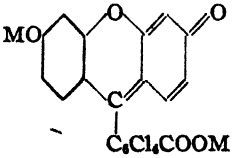
I. Tetrachlorofluorescein monobenzoate (colorless).



II. Tetrachlorofluorescein monobenzoate and its sodium salt (colored).

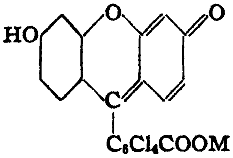
of two phenolic hydroxyl groups in tetrachlorofluorescein and as the compound is colorless and insoluble in alkalies it must have the lactoid structure and be represented by a formula similar to that on p. 715.

The dipotassium, disodium, and diammonium salts of tetrachlorofluorescein, because of their color, are considered to be derivatives of the quinoid form of tetrachlorofluorescein, and may be represented by the following general formula, where M represents the metal or the NH_4 group:



Di-metallic salts of tetrachlorofluorescein.

The colored monopotassium and monosodium salts and the red methyl ester are also derivatives of the quinoid form and may be represented by the general formula, where M represents the metal or the CH_3 group:

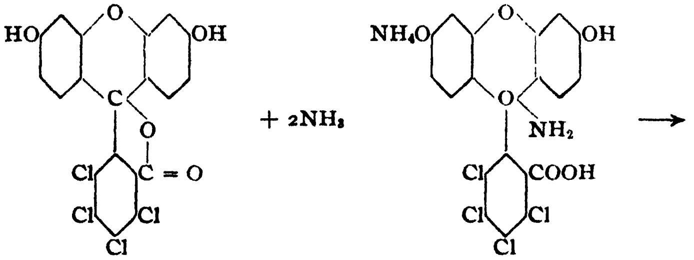


Mono-metallic salts and esters of tetrachlorofluorescein.

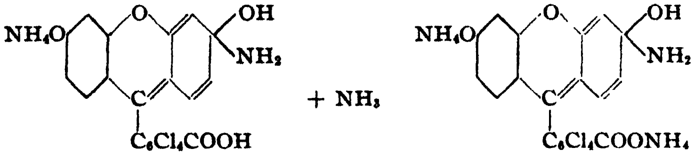
When dry ammonia acts upon the red anhydrous form of tetrachlorofluorescein, a diammonium salt is formed, which must be represented by the formula previously given for the di-metallic salts. When, however, the colorless anhydrous tetrachlorofluorescein is placed in a current of *dry* ammonia, an equivalent of *three* molecules of ammonia is absorbed, and a colored triammonia salt results. The diammonium salt loses all of its ammonia when heated to a temperature of 150°, and the *dark red*, anhydrous tetrachlorofluorescein remains, but when the colored triammonia salt is heated to the same temperature, all of the ammonia is lost and the *colorless* anhydrous tetrachlorofluorescein is obtained.

The formation of the triammonia salt may be represented in either of the following ways:

First method:



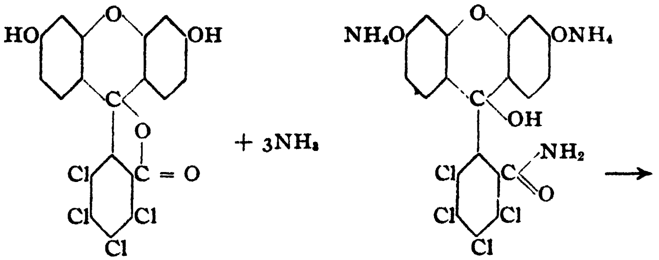
Tetrachlorofluorescein (colorless).



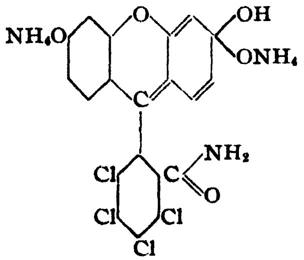
Triammonia salt of tetrachlorofluorescein.

(I)

Second method:



Tetrachlorofluorescein (colorless).



Triammonia salt of tetrachlorofluorescein.

(II)

The second method of formation is more in accord with the action of ammonia on certain lactones. Neugebauer[1] has found that the lactone of γ-hydroxyvaleric acid is converted into the amide according to the following reaction:

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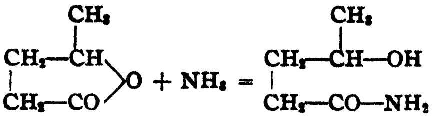
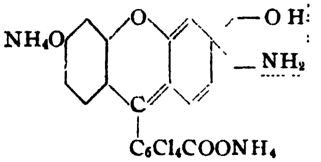
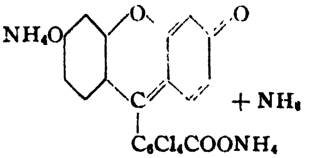
[1] *Ann.*, **227**, 103 (1885); also **256**, 147 (1889).



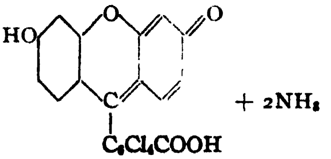
The second method of formation also seems the more probable from the fact that a triammonia salt having a structure represented by Formula II could lose three molecules of ammonia and form the lactoid modification of tetrachlorofluorescein—the steps of the formation being reversed. While a triammonia salt having a structure represented by Formula I would, upon the loss of one molecule of ammonia, probably be converted into the red diammonium salt of tetrachlorofluorescein. This diammonium salt would, as already shown, lose all of its ammonia upon heating and be converted into the red anhydrous tetrachlorofluorescein. This transformation may be represented as follows:



Triammonia salt of Tetrachlorofluorescein. (I)

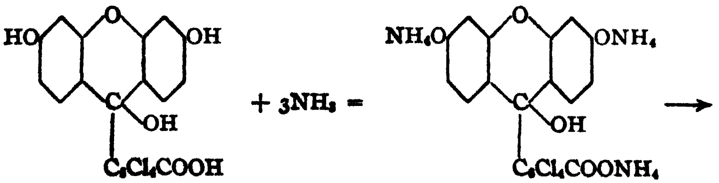


Diammonium salt of Tetrachlorofluorescein

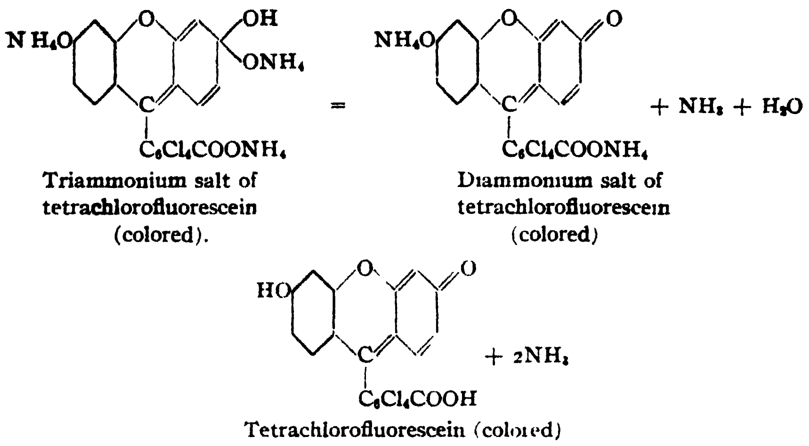


Tetrachlorofluorescein (colored).

This theory is further confirmed by the behavior of tetrachlorofluoresceincarbinolcarboxylic acid toward dry ammonia. This compound takes up an equivalent of *three* molecules of ammonia without loss of water, and when the salt thus formed is heated both water and ammonia are given off, and the red anhydrous tetrachlorofluorescein is obtained. These changes may be represented as follows:



Tetrachlorofluoresceincarbinolcarboxylic acid.

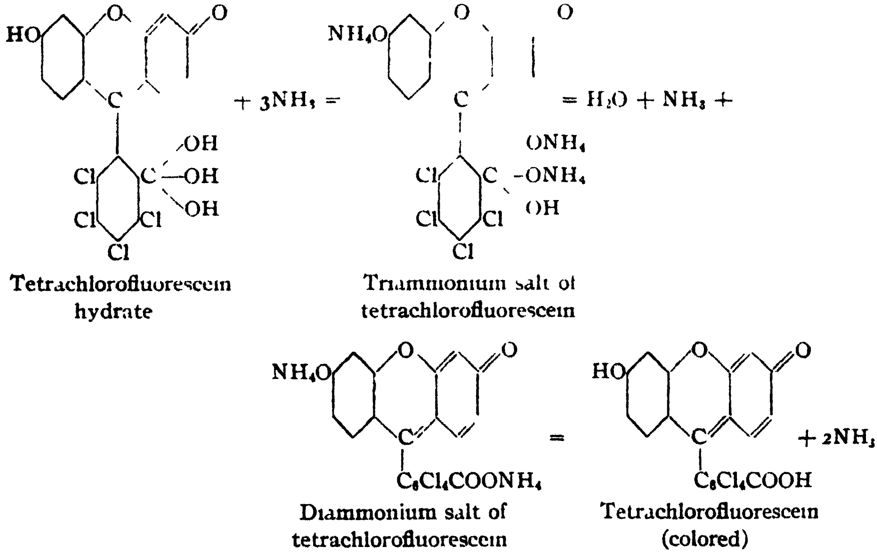


Triammonium salt of tetrachlorofluorescein (colored).

Diammonium salt of tetrachlorofluorescein (colored)

Tetrachlorofluorescein (colored)

The yellow hydrate when placed in dry ammonia also absorbs three molecules of ammonia without the loss of water. When this salt is heated both ammonia and water are lost, and the red anhydrous tetrachlorofluorescein is formed. These steps in the formation of this triammonium salt and its transformation when heated may be represented as follows·



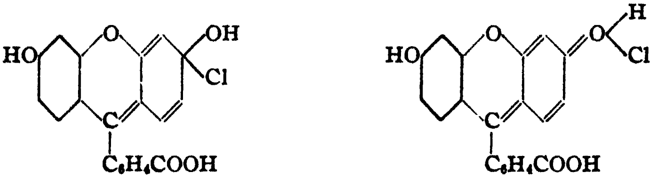
Tetrachlorofluorescein hydrate

Triammonium salt of tetrachlorofluorescein

Diammonium salt of tetrachlorofluorescein

Tetrachlorofluorescein (colored)

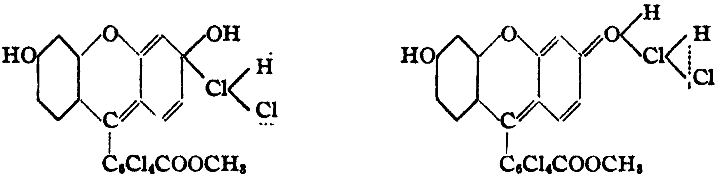
The behavior of this hydrate toward ammonia shows that the introduction of the four chlorine atoms into the phthalic acid residue of fluorescein increases its acid and decreases its basic properties. This is also shown by the fact that tetrachlorofluorescein is unchanged by boiling with concentrated hydrochloric acid, while fluorescein is converted into the hydrochloride by this treatment. When placed in dry hydrochloric acid gas, *fluorescein* also absorbs one molecule of hydrochloric acid and is converted into the hydrochloride (see p. 701), while neither the quinoid nor the lactoid form of tetrachlorofluorescein will absorb hydrochloric acid under these conditions. The hydrochloride of *fluorescein* may be regarded as either a carbonium or oxonium salt (Formulas I and II).



I. Carbonium salt. II. Oxonium salt.

Fluorescein hydrochloride.

The methyl ester of tetrachlorofluorescein, like the esters of tetrachlorogallein,[1] dissolves in hydrochloric acid (sp. gr. 1.10) with the formation of a hydrochloride. When this ester is treated with dry hydrochloric acid gas an equivalent of almost two molecules is absorbed. This dihydrochloride may be regarded as a carbonium or an oxonium salt as shown in Formulas I and II.

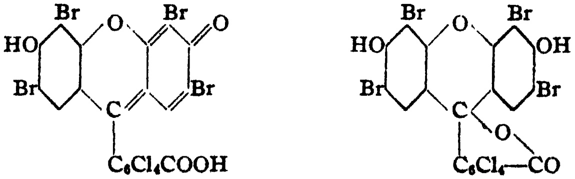


I. Carbonium salt. II. Oxonium salt.

Tetrachlorofluorescein methyl ester dihydrochloride.

Such a compound would lose one molecule of hydrochloric acid quite readily to form the monohydrochloride as shown above (see p. 700).

Tetrachloroeosin is similar, in many respects, to eosin. It forms two classes of derivatives, one colored, the other colorless. The colored compounds are regarded as derived from the quinoid form I, while the colorless compound must have the lactoid structure and be derivatives of the lactoid form II.



I. Quinoid form (colored). II. Lactoid form (colorless).

Tetrachloroeosin.

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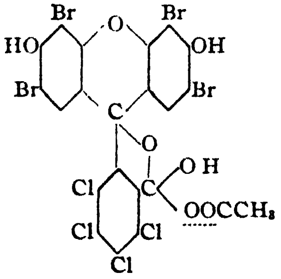
[1] *Am. Chem. J.*, 42, 258 (1909).

As examples of the first class there have been prepared, tetrachloroeosin hydrate (pink), and the dipotassium salt of tetrachloroeosin (dark red). The white diacetate and the compound with acetic acid are examples of the colorless lactoid derivatives of tetrachloroeosin.

When tetrachloroeosin is crystallized from glacial acetic acid a compound of tetrachloroeosin with acetic acid is formed. Since this substance is colorless and loses one molecule of acetic acid when heated, and gives the colorless tetrachloroeosin, it may be represented by the lactoid formula,



Compound of tetrachloroeosin with acetic acid.

It is interesting to note the effect of the introduction of substituents into the benzene nuclei of fluorescein upon the relative stability of the two possible forms of the free phthalein. Fluorescein in the free state exists only in the *colored* quinoid form. No colorless free fluorescein has ever been prepared. Tetrachlorofluorescein, on the other hand, has been obtained in two modifications, *colored* and *colorless*, but the colored form is the more stable. Eosin in the free state is flesh-colored, and may be a mixture of the two forms, while the free tetrachloroeosin is *colorless*, or only very slightly colored. The colored modification has not yet been prepared.[1]

Tetrachloroeosin, like tetrachlorofluorescein, does not absorb hydrochloric acid gas, nor is it changed by boiling with concentrated hydrochloric acid. That it is a much stronger acid than tetrachlorofluorescein is shown by its conduct toward ammonia. When placed in dry ammonia, the colorless tetrachloroeosin absorbs an equivalent of five molecules of ammonia, while the colorless tetrachlorofluorescein absorbs only three. When the red salt formed by the action of ammonia upon tetrachloroeosin is heated to 150°, all of the ammonia is lost and the colorless tetrachloroeosin remains. The formation of this compound from the white tetrachloroeosin and its transformation back into the white tetrachloroeosin may be represented as follows:

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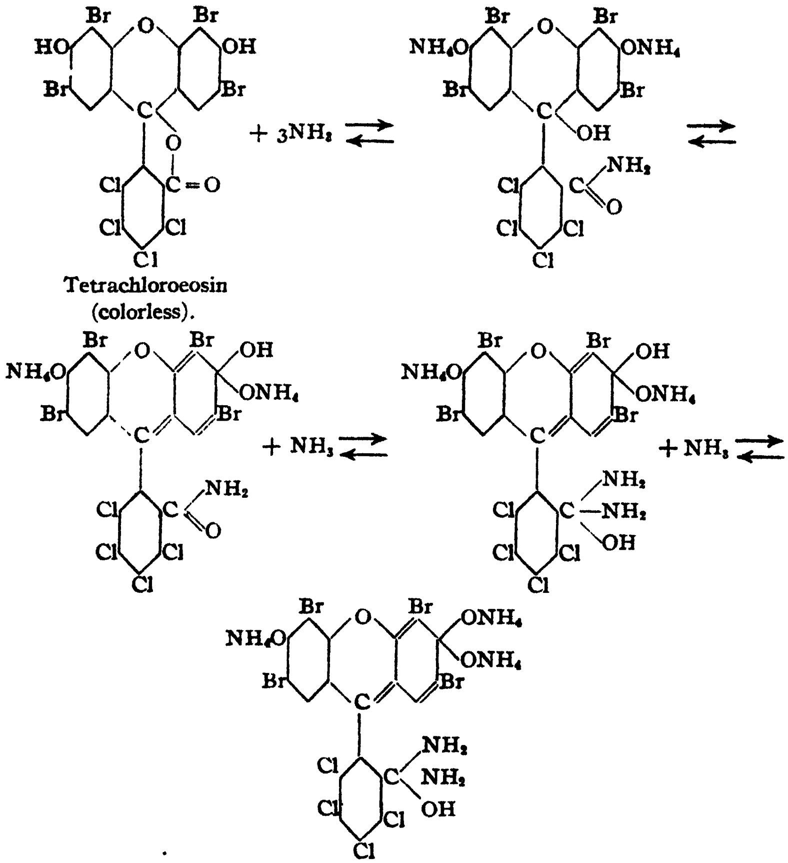
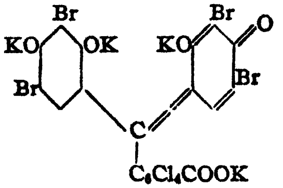
[1] The dark-red solution of tetrachloroeosin in nitrobenzene may contain the quinoid modification.



Tetrachloroeosin (colorless).

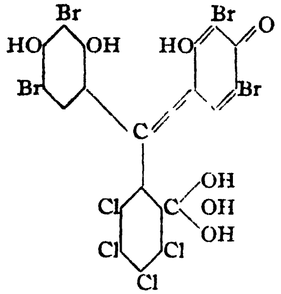
That the ammonia does not add to the pyrone oxygen to form a salt analogous to the tetrapotassium salt is shown by the fact that this ammonium salt dissolves in water with the pink color and greenish fluorescence so characteristic of tetrachloroeosin. The pink compound which precipitates when the aqueous solution of the *blue* tetrapotassium salt is acidified, dissolves in ammonia with a *blue* color and no fluorescence.

The increased acidity of tetrachloroeosin over tetrachlorofluorescein is also shown by the indications of the formation of a tetrapotassium salt when tetrachloroeosin is treated with a strong solution of potassium hydroxide (see p. 704). This salt would probably have the structure,



Tetrapotassium salt of tetrachloroeosin.

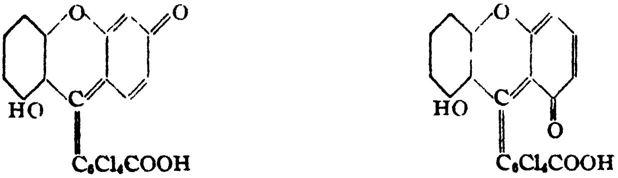
The pink compound formed when this strong alkaline solution is poured into an excess of acid would probably contain three phenolic hydroxyl groups and be represented by the formula:



This is a tetrabromo derivative of the true resorcinoltetrachlorophthalein hydrate.

That tetrachloroeosin is a stronger acid than tetrachlorofluorescein is also shown by the fact, stated on p. 706, that some of the disodium salt is always formed when tetrachloroeosin is treated with an alcoholic solution of sodium acetate. When tetrachlorofluorescein is treated with this reagent only the monosodium salt results.

The two isomers of tetrachlorofluorescein, Formulas I and II, have not yet been isolated. The very *dark red* material which was obtained from the crude product, and which dissolves in alkalies with a deep red color and an intense greenish fluorescence (see p. 686) may be a mixture of both of these isomers.



(I) (II)

Isomeric tetrachlorofluoresceins

The absorption spectra of solutions of fluorescein, tetrachlorofluorescein, eosin, and tetrachloroeosin show in a marked degree the influence of the introduction of halogen substituents into the benzene nuclei of fluorescein. It will be noted that, in passing from fluorescein to tetrachloroeosin in the order named above, the absorption bands are gradually shifted towards the red end of the spectrum, and that this shifting is approximately proportional to the number of halogen atoms introduced rather than to the increase in the molecular weight of the compounds. For example, the absorption bands of tetrachlorofluorescein and eosin are practically identical while the molecular weights of these substances are 470 and 648, respectively.

The wave lengths of the crests of the fluorescence bands show a very interesting relation to the number and atomic weights of the halogens introduced. The introduction of *four chlorine* atoms into *one* benzene ring increases the wave length approximately the same amount as when *four bromine* atoms are introduced into *two* benzene rings. It is interesting to note that these increases in wave lengths are almost exactly in the ratio 4 Cl : 2 Br. For example, the difference between the wave length of the band for fluorescein and that for tetrachlorofluorescein is 24, and the difference for fluorescein and eosin is 28. This ratio, 24 : 28, or 6 : 7, is very nearly the same as that of 4 Cl : 2 Br, which is 6 : 6.76.

These results seem to confirm the theory that the seat of the fluorescence lies in the benzene ring, and that the introduction of substituents and the position these occupy in the molecule, brings the fluorescence within the visible part of the spectrum. The fact noted by Professors Nichols and Merritt that the more intense absorption band in the case of tetrachlorofluorescein, eosin and tetrachloroeosin is *double* would also seem to show that the absorption was due to the condition existing in the benzene ring for there are three absorption bands and three benzene rings.

Summary.

The results of this investigation may briefly be stated as follows:

1. Tetrachlorofluorescein has been prepared in two modifications, a *colored quinoid*, and a *colorless lactoid* form.

2. A colorless diacetate, a colorless dibenzoate, a colorless monobenzoate of tetrachlorofluorescein and a colorless acetate of this benzoate and colorless compounds of tetrachlorofluorescein with ether and with ethyl acetate have been prepared. These are all derivatives of the *lactoid* form of tetrachlorofluorescein.

3. The dipotassium, disodium, diammonium, monopotassium and monosodium salts, the hydrate and the methyl ester of tetrachlorofluorescein have been prepared. All of these compounds are colored and are therefore derivatives of the *quinoid* form of tetrachlorofluorescein.

4. A colorless carbinol carboxylic acid of tetrachlorofluorescein has been prepared. This substance is isomeric with the *yellow* hydrate, but forms the same *colored* salts with alkalies, and the same *colorless* diacetate as is obtained from this hydrate and from the anhydrous modifications of tetrachlorofluorescein.

5. The introduction of the four chlorine atoms into the fluorescein molecule increases its acid and decreases its basic properties. This is shown by the conduct of tetrachlorofluorescein toward hydrochloric acid and toward gaseous ammonia, as compared with that of fluorescein itself.

6. Tetrachloroeosin, which is the tetrabromo derivative of tetrachlorofluorescein, its compound with acetic acid, and its diacetate have been

made. These are all colorless compounds and therefore have the lactoid structure. Tetrachloroeosin itself has only been obtained in the *colorless lactoid* modification.

7. As examples of the derivatives of the colored quinoid form of tetrachloroeosin, the hydrate and the dipotassium salt have been prepared.

8. The introduction of four bromine atoms into the molecule of tetrachlorofluorescein increases the acidity of the compound, as is shown by the behavior of tetrachloroeosin toward gaseous ammonia and toward strong solutions of the alkalies.

9. Indications of the existence of the two possible isomeric tetrachlorofluoresceins have been obtained.

10. The absorption and fluorescence spectra of solutions of fluorescein tetrachlorofluorescein, eosin, and tetrachloroeosin have been studied. The theory of Stark and Meyer and of Kauffmann that the benzene nucleus is the seat of fluorescence, is apparently confirmed.

ITHACA, N. Y.

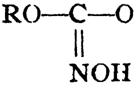
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

OXIMIDOCARBONIC ESTERS AND RELATED COMPOUNDS.

BY LAUDER WILLIAM JONES AND RALPH E. OESPER.

Received February 20, 1914.

The experiments described in this paper were begun several years ago, but were interrupted before any definite conclusions were arrived at. Some time ago, the work was resumed; and, in view of the fact that, recently, Houben and Schmidt[1] have published an account of experiments in which they have duplicated some of our unpublished results, it seemed desirable that a preliminary announcement of our experiments should appear at this time.

The oximidocarbonic esters, *i. e.*, compounds of the formula  $RO—\underset{\underset{NOH}{\|}}{C}—OR$, may be of two types: simple esters in which the two radicals are alike; and mixed esters in which they are different. The latter type is especially interesting, since it offers the possibility of obtaining geometrical stereoisomers in *syn*- and *anti*-modifications. This work was undertaken in the hope of isolating these stereoisomers, and, also, with the intention of investigating their behavior when they are subjected to the action of reagents which bring about the Beckmann rearrangement of oximes, etc.

We found that the preparation of the simple oximido esters offered no special difficulties, since they could be obtained from imidocarbonic esters by the action of hydroxylammonium chloride.

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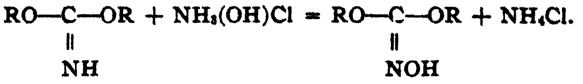
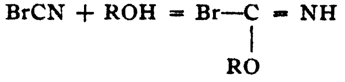
[1] Houben and Schmidt, *Ber.*, 46, 2458 (1913).



$$\underset{\text{NH}}{\text{RO—}\overset{}{\underset{\|}{\text{C}}}\text{—OR}} + NH_3(OH)Cl = \underset{\text{NOH}}{\text{RO—}\underset{\|}{\text{C}}\text{—OR}} + NH_4Cl.$$

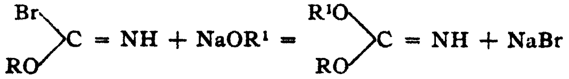
By this method Houben and Schmidt have recently prepared the diethyl and the dimethyl derivatives. The simple imidocarbonic esters are obtained by the action of bromocyanogen on a mixture of an alcohol and its sodium alcoholate. This reaction may be represented by the following equations:

(I)



$$BrCN + ROH = Br\text{—}\underset{\substack{|\\ RO}}{C} = NH$$

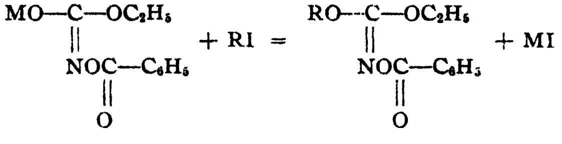
(II)



$$\genfrac{}{}{0pt}{}{Br}{RO}{>}C = NH + NaOR^1 = \genfrac{}{}{0pt}{}{R^1O}{RO}{>}C = NH + NaBr$$

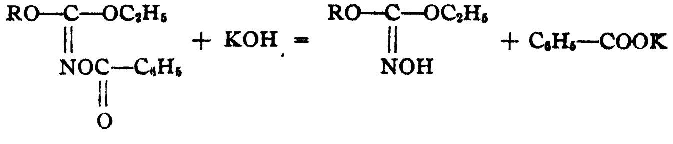
In this way Nef[1] prepared the diethyl and diphenyl esters, and Hantzsch[2] the di-*p*-bromophenyl ester. When sodium phenolate was allowed to react with bromocyanogen in the presence of ethyl alcohol, Nef[3] observed that the ethylphenyl ester, as well as the diphenyl derivative, resulted. This is obvious, since any alcohol may take part in the second stage of the process represented above. At first glance this would seem to afford a method of preparing the mixed imidocarbonic esters, but a mixture of two, and possibly three, substances might result, and their separation would be practically impossible, since these compounds cannot be distilled without considerable decomposition.

It seemed probable that the mixed oximido esters might be prepared by the following method: The salts of the acyl derivatives of hydroxyurethane,[4] when treated with alkyl halides, might be expected to give acylated oximidocarbonic esters:



$$\begin{array}{l}MO\text{—}C\text{—}OC_2H_5\\ \quad\ \|\\ \quad NOC\text{—}C_6H_5\\ \qquad\|\\ \qquad O\end{array} + RI = \begin{array}{l}RO\text{—}C\text{—}OC_2H_5\\ \quad\ \|\\ \quad NOC\text{—}C_6H_5\\ \qquad\|\\ \qquad O\end{array} + MI$$

On careful hydrolysis with alkalies, the acyl radical might be eliminated:



$$\begin{array}{l}RO\text{—}C\text{—}OC_2H_5\\ \quad\ \|\\ \quad NOC\text{—}C_6H_5\\ \qquad\|\\ \qquad O\end{array} + KOH = \begin{array}{l}RO\text{—}C\text{—}OC_2H_5\\ \quad\ \|\\ \quad NOH\end{array} + C_6H_5\text{—}COOK$$

However, the acylated derivative of hydroxyurethane may exist in two possible tautomeric forms:

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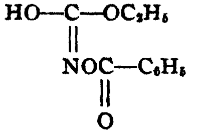
[1] Nef, *Ann.*, **287**, 313, 319 (1895).

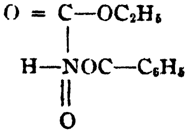
[2] Hantzsch and Mai, *Ber.*, **28**, 2469 (1895).

[3] Nef, *Loc. cit.*, 321.

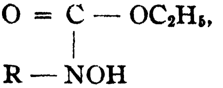
[4] Jones, *Am. Chem. J.*, **20**, 49 (1898).

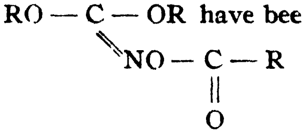
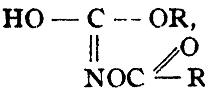
(I) 

$$\begin{array}{l} HO-C-OC_2H_5 \\ \quad\;\| \\ \quad NOC-C_6H_5 \\ \qquad\;\| \\ \qquad O \end{array}$$

(II) 

$$\begin{array}{l} O = C-OC_2H_5 \\ \qquad\;| \\ H-NOC-C_6H_5 \\ \qquad\quad\| \\ \qquad\quad O \end{array}$$

If the *silver salts* correspond to Formula (I), then the reaction outlined above would lead to the desired compounds; but if they react according to type (II) isomeric derivatives,  $\begin{array}{l} O = C - OC_2H_5, \\ \quad\;\;| \\ R - NOH \end{array}$ would be obtained.

When such possibilities exist, the silver salt usually gives compounds in which the alkyl group is bound chiefly to oxygen, while the sodium salt leads to the corresponding nitrogen derivative. In the cases investigated so far, *viz.*, those in which the ethyl group or the isoamyl group was introduced, we have found that the silver salts gave rise to *nitrogen esters;* the resulting compounds, when hydrolyzed with hydrochloric acid, yielded β-substituted hydroxylamines, which proved that the alkyl group was bound to nitrogen. Under the same treatment, the isomeric oxygen derivatives would have yielded hydroxylamine itself. Furthermore, compounds of the form  $\begin{array}{l} RO - C - OR \\ \qquad\;\diagdown \\ \qquad\;\; NO - C - R \\ \qquad\qquad\quad\| \\ \qquad\qquad\quad O \end{array}$ have been prepared, and were found to be crystalline solids, while the nitrogen alkyl derivatives obtained by us were oils, which did not solidify even when cooled to —20°. It is possible that moist silver oxide may form silver salts with the "metal bound to oxygen," just as Tafel and Enoch[1] have assumed to be the case for amides; or that some of the other compounds of the type,  $\begin{array}{l} HO - C - OR, \\ \quad\;\;\| \\ \quad NOC{\overset{\diagup\!\!\diagup O}{\underset{}{\diagdown R}}} \end{array}$ may give the desired mixed oximido esters. Then again, it may be that the oxygen esters actually were formed first, and that the conditions of our experiments have not been chosen properly to prevent their rearrangement to N-esters, in much the same way that imido esters[2] have been formed to rearrange to give alkyl amides. After these compounds have been investigated more fully, our results will be presented in a later article.

When the *sodium salt* of the benzoyl ester of hydroxyurethane was allowed to react with ethyl iodide in the presence of alcohol, a liquid was obtained which boiled constantly within one degree. But the figures of the analysis did not agree with the values calculated for the ethyl derivative; and, on investigation, the liquid was found to be a mixture of *o*-ethyl hydroxyurethane and benzoic ethyl ester. During the process, alcoholysis had taken place to give the sodium salt of hydroxyurethane and benzoic ethyl ester, and the reaction had proceeded as follows:[1]

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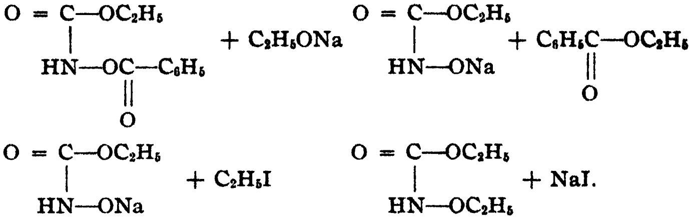
[1] Tafel and Enoch, *Ber.*, 23, 104 (1890); Meyer and Jacobson, *Lehrbuch*, Vol. I, p. 615.

[2] Comstock and Wheeler, *Am. Chem. J.*, 13, 522 (1891); Wheeler, 21, 1865 (1899); 23, 140 (1901).

(I)
(II)

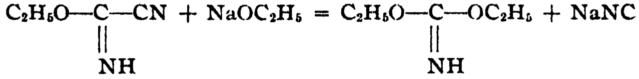


$$\text{(I)}\quad \mathrm{O{=}C(\text{—}OC_2H_5)\text{—}HN\text{—}OC({=}O)\text{—}C_6H_5} + \mathrm{C_2H_5ONa} \qquad \mathrm{O{=}C(\text{—}OC_2H_5)\text{—}HN\text{—}ONa} + \mathrm{C_6H_5C({=}O)\text{—}OC_2H_5}$$

$$\text{(II)}\quad \mathrm{O{=}C(\text{—}OC_2H_5)\text{—}HN\text{—}ONa} + \mathrm{C_2H_5I} \qquad \mathrm{O{=}C(\text{—}OC_2H_5)\text{—}HN\text{—}OC_2H_5} + \mathrm{NaI}.$$

The action of the alcohol-free salt will be studied later. However, since the silver salts gave nitrogen alkyl derivatives, the sodium salts will probably do the same, so that this method, in its present form at least, does not seem to be practicable for the preparation of the oximidocarbonic esters.

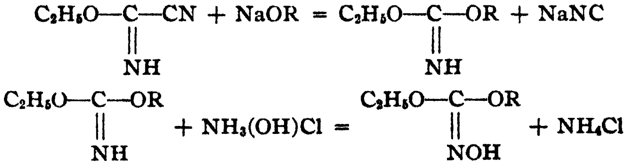
A reaction described by Nef[2] offered a method for the preparation of the mixed imidocarbonic esters. By the action of sodium ethylate on cyanimidocarbonic ethyl ester, he obtained imidocarbonic ethyl ester.



$$\mathrm{C_2H_5O\text{—}C({=}NH)\text{—}CN + NaOC_2H_5 = C_2H_5O\text{—}C({=}NH)\text{—}OC_2H_5 + NaNC}$$

By using other alcoholates in place of sodium ethylate, the desired imido compounds may be obtained, which, on treatment with hydroxylammonium chloride, would give the mixed oximidocarbonic esters.

Thus:



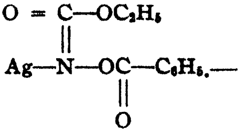
$$\mathrm{C_2H_5O\text{—}C({=}NH)\text{—}CN + NaOR = C_2H_5O\text{—}C({=}NH)\text{—}OR + NaNC}$$

$$\mathrm{C_2H_5O\text{—}C({=}NH)\text{—}OR + NH_3(OH)Cl = C_2H_5O\text{—}C({=}NOH)\text{—}OR + NH_4Cl}$$

Experimental Part

Derivatives of Hydroxyurethane.

The Silver Salt of the Benzoyl Ester of Hydroxyurethane,



$$\mathrm{Ag\text{—}N(\text{=}C(\text{—}OC_2H_5){=}O)\text{—}OC({=}O)\text{—}C_6H_5}.\text{—}$$

Seven and four-tenths grams of sodium hydroxide were mixed with 37 g. of the benzoyl ester of hydroxyurethane dissolved in alcohol, and 30 g. of silver nitrate dissolved in water were added. The heavy, yellow precipitate was separated by filtration, washed with a small amount of water, and then with alcohol. It was dried on a clay plate placed in an amber desiccator. The salt is rather sensitive to light and is best prepared in the dark.

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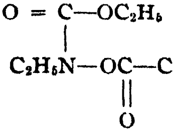
[1] Compare Titherly, *J. Chem. Soc.*, 79, 392 (1901).

[2] Nef, *Loc. cit.*, p. 286.

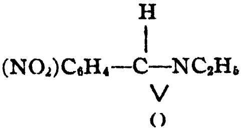
Preparation of the N-Ethyl Derivative of the Benzoyl Ester of Hydroxyurethane,  $C_2H_5N(-C(=O)-OC_2H_5)-OC(=O)-C_6H_5$.—Twenty-seven grams of ethyl iodide were added to 50 g. of the silver salt suspended in ether, and the mixture was allowed to stand in the dark for two weeks. At the end of this time the bright yellow color of the silver salt had disappeared. The silver iodide was separated by filtration and washed with ether. After shaking the ether solution with a solution of sodium thiosulfate to remove the small quantity of iodine that had separated, it was dried with fused sodium sulfate and freed from ether by distillation. The light yellow oil which remained was fractionated *in vacuo.* After three fractionations, 10 g. were obtained which boiled with slight decomposition between 188–190°, under a pressure of 25 mm.

0.1526 g. gave 8.64 cc. N_2 at 29° and 743 mm.

Calc. for $C_{12}H_{15}O_4N$: N, 5.90. Found, N, 6.09.

The substance was an oil with a spicy odor. It was nearly insoluble in water, but soluble in most organic solvents.

Hydrolysis of the Ethyl Derivative by Hydrochloric Acid.—Three and seven-tenths grams of the oil were heated with 10 cc. of concentrated hydrochloric acid in a sealed tube for six hours at 105°. When the tube was opened, carbon dioxide and ethyl chloride escaped. The contents of the tube were extracted wlth ether, and 1.4 g. (calculated 1.5 g.) of benzoic acid were obtained when the ether was evaporated. The water solution was concentrated over a water bath until a thick yellow oil remained which would not solidify even at —10°. It was identified as β-ethyl hydroxylammonium chloride by condensing it with para-nitrobenzaldehyde. The condensation product melted at 123°, which agrees with the value given by Hantzsch[1] for N-ethyl-*p*-nitroisobenzaldoxime,



$$(NO_2)C_6H_4-\overset{H}{\overset{|}{C}}\underset{\underset{O}{\vee}}{-}NC_2H_5$$

Therefore, the ethyl group was bound to nitrogen, since hydroxylamine would have been produced by the hydrolysis of the ethoxy derivative. The hydrolysis may be represented as follows:

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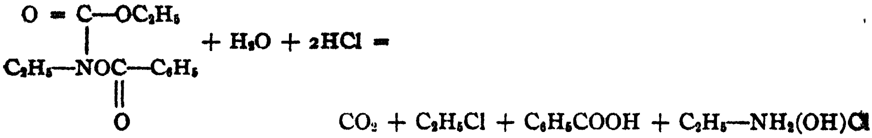
[1] Hantzsch and Hillard, *Ber.*, 31, 2066 (1898).



$$\begin{array}{l} O = C\text{—}OC_2H_5 \\ \quad\;\, | \\ C_2H_5\text{—}NOC\text{—}C_6H_5 \\ \qquad\quad \| \\ \qquad\quad O \end{array} + H_2O + 2HCl = CO_2 + C_2H_5Cl + C_6H_5COOH + C_2H_5\text{—}NH_2(OH)Cl$$

The Action of Ethyl Iodide on the Sodium Salt of the Benzoyl Ester of Hydroxyurethane.—To a solution of 35 g. of benzoyl ester of hydroxyurethane in alcohol, 3.8 g. of sodium, dissolved in alcohol, and 26 g. of ethyl iodide were added. After two weeks the alcohol was removed by distillation and the mixture of oil and crystals which remained was extracted with ether. After washing the ether with water, it was dried with sodium sulfate and distilled. A colorless oil was obtained which was fractionated *in vacuo*, 24 g. of a clear colorless liquid, boiling at 108–109° at 25 mm., resulting.

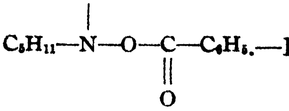
The figures which the analysis of the oil gave did not agree with the values calculated for the ethyl derivative; and, on a further investigation, it was found that the oil consisted of a neutral and an acid portion. It was dissolved in ether and shaken with a solution of sodium hydroxide. The neutral portion was found to be ethyl benzoate, boiling at 213°. The alkaline solution was acidified and extracted with ether. A clear, colorless liquid was obtained which boiled between 96–7° at 17 mm. When treated with phosphorus pentachloride and then with water and alkalies, it gave a base whose chloride melted at 127°. This chloride formed a chloroplatinate which melted with decomposition between 174–176°.

0.096 g. gave 0.0352 g. Pt.

Calc. for $(C_2H_5ONH_3)_2PtCl_6$: Pt, 36.65. Found: Pt, 36.66.

These results showed that the compounds under consideration were derivatives of α-ethylhydroxylamine.

The acid portion was therefore *o*-ethyl hydroxyurethane. It was found to be identical with the ethyl derivative described by Jones.[1] The origin of these products was explained above.

Preparation of N-Isoamyl Derivative of the Benzoyl Ester of Hydroxyurethane, 

$$\begin{array}{l} O = C\text{—}OC_2H_5 \\ \qquad\;\; | \\ C_5H_{11}\text{—}N\text{—}O\text{—}C\text{—}C_6H_5 \\ \qquad\qquad\quad\;\, \| \\ \qquad\qquad\quad\;\, O \end{array}$$

.—Eleven and nine-tenths grams of isoamyl iodide were added to 19 g. of the silver salt of the benzoyl ester of hydroxyurethane suspended in ether. After two weeks the silver iodide was removed and the product was treated in the manner described under the ethyl derivative. After three fractionations, 16 g. of a yellow oil, boiling, with slight decomposition, between 203–205° at 30 mm., were obtained.

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[1] Jones, *Loc. cit.*, p. 46.

0.1562 g. gave 7.9 cc. N_2 at 31° and 745 mm. Calc. for $C_{15}H_{21}O_4N$: N, 5.01. Found: N, 5.10.

The substance resembled the ethyl derivative described above in all of its properties.

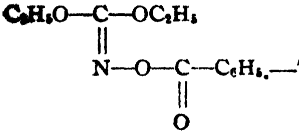
The Hydrolysis of the N-Isoamyl Derivative with Hydrochloric Acid.—Three grams of the oil were heated with 10 cc. of concentrated hydrochloric acid in a sealed tube for three hours at 110°. Carbon dioxide and ethyl chloride escaped on opening the tube. One and two-tenths grams of benzoic acid (calculated 1.3 g.) were extracted with ether and the water gave brownish crystals when evaporated. These crystals were dissolved in alcohol and a turbid suspension was produced by the addition of ether. An alcoholic solution of platinic chloride precipitated a yellow solid substance, which was analyzed.

0.0960 g. gave 0.0310 g. of Pt. Calc. for $(C_5H_{11}NH_2OH)_2PtCl_6$: Pt, 31.63. Found: Pt, 32.29.

In this case, also, the alkyl group was bound to nitrogen.

Derivatives of Oximidocarbonic Esters.

Preparation of the Benzoyl Ester of Oximidocarbonic Ethyl Ester,



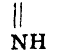
$$\begin{array}{l} C_2H_5O\text{—}C\text{—}OC_2H_5 \\ \qquad\;\;\; \| \\ \qquad\;\;\; N\text{—}O\text{—}C\text{—}C_6H_5 \\ \qquad\qquad\qquad\;\; \| \\ \qquad\qquad\qquad\;\; O \end{array}$$

—Three and one-tenth grams of sodium bicarbonate were added to 5 g. of oximidocarbonic ethyl ester[1] dissolved in 10 g. of water. Five and one-tenth grams of benzoyl chloride were added in small portions, the flask being cooled with running water. A colorless oil separated which soon solidified to a mass of white crystals. These were collected on a filter, dried, and recrystallized from chloroform and ligroin. They formed fine needles which melted at 148°.

0.2716 g. gave 14.9 cc. N_2 at 29° and 745 mm. Calc. for $C_{12}H_{15}O_4N$: N, 5.90. Found: N, 5.91.

The compound was soluble in benzene, in alcohol and in chloroform, not very soluble in ether, and insoluble in ligroin and in water. Several crystals were added to the ethyl derivative obtained from the silver salt described above, but the oil showed no tendency to solidify, which proved that the latter was not the oxygen ester existing as an undercooled liquid.

Preparation of Imidocarbonic Ethyl Isoamyl Ester,



$$\begin{array}{l} C_2H_5O\text{—}C\text{—}OC_5H_{11} \\ \qquad\quad\; \| \\ \qquad\quad NH \end{array}$$

.—Five and three-tenths grams of sodium were treated with the equivalent quantity (20 g.) of isoamyl alcohol in the presence of ether.[2] Twenty-two and five-tenths grams of cyanimidocarbonic ethyl ester, prepared from bromocyanogen, potassium cyanide, and alcohol[1] were added to the suspended alcoholate. Heat was developed, the solution became yellow, and sodium cyanide was precipitated. The reaction mixture was heated for two hours in a flask connected with a reflux condenser, and enough water was added to dissolve the sodium cyanide. After the water solution had been extracted with ether several times, the ether was dried with calcium chloride. Thus, 32 g. of a light yellow oil, possessing a strong basic odor, were obtained when the ether was evaporated. Even at a pressure of 25 mm. the compound could not be distilled without considerable decomposition. Therefore, no analysis of the substance was attempted. Its identity was established by converting it into the corresponding oximido derivative.

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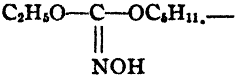
[1] Houben and Schmidt, *Loc cit.*

[2] Brühl, *Ber.*, 37, 2066 (1904)

Preparation of Oximidocarbonic Ethyl Isoamyl Ester,



$C_2H_5O—\underset{NOH}{\underset{\|}{C}}—OC_5H_{11}$.—

Eight and four-tenths grams of hydroxylamine, dissolved in a small amount of water, were added to 20 g. of the imido ester dissolved in 20 cc. of ether. The mixture was shaken thirty minutes, the water layer was drawn off, extracted several times with ether, and the ether dried with sodium sulfate. Twenty grams of a reddish yellow oil were obtained when the ether evaporated. When cooled to —15°, white crystals appeared which melted when they were spread out on a cold clay plate.

0.1754 g. gave 12.8 cc. N_2 at 24.5° and 742 mm. Calc. for $C_8H_{17}O_3N$: N, 7.99. Found: N, 8.01.

When freshly prepared, the substance was practically odorless but, on standing, the odor of isoamyl alcohol became apparent. The oil was insoluble in water, but soluble in alkalies, and in most organic solvents.

CINCINNATI, OHIO.

FRIEDEL AND CRAFTS' REACTION—THE PREPARATION OF ORTHOBENZOYL-BENZOIC ACID AND BENZOPHENONE.

By C. R. Rubidge and N. C. Qua.

Received February 20, 1914.

Orthobenzoyl-benzoic acid had been prepared by several investigators but was first prepared by means of the reaction between phthalic anhydride, benzene and aluminium chloride, by Friedel and Crafts.[2] Heller[3] showed that the aluminium chloride was not a catalytic agent and that a good yield depended on the phthalic anhydride and the aluminium chloride being used in the proportion of their formula weights(using Al_2Cl_6).

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[1] Nef, *Loc. cit.*, p. 293.

[2] *Ann. chim. phys.*, [6] 14, 446 (1888).

[3] *Z. angew. Chem.*, 19, 669 (1906).

In a later article Heller and Shülke[1] suggested that the reaction might be represented as taking place in two stages:

$C_8H_4O_3 + C_6H_6 + Al_2Cl_6 \longrightarrow C_8H_4O_3Al_2Cl_6C_6H_6 \longrightarrow C_{14}H_9O_3Al_2Cl_5 + HCl$, the latter compound with hydrochloric acid giving orthobenzoyl-benzoic acid. Heller obtained a yield of 93%, or counting in the recovered phthalic acid 97%, and in two experiments obtained 0.87 mol and 0.93 mol, respectively, of hydrogen chloride for each mol of phthalic anhydride used. Heller also states that if one-half the usual amount of aluminium chloride is used the yield is reduced to less than one-half.

The following experiments on the preparation of orthobenzoyl-benzoic acid and benzophenone, using varying quantities of the reagents, were begun by the first named author and finished by the second.

The aluminium chloride used was Kahlbaum's "sublimed" and had been kept in sealed bottles in the laboratory for more than a year; preliminary experiments showed that this gave as good yields as were obtained when the aluminium chloride had been freshly sublimed. The phthalic anhydride and benzene were obtained from the same firm but it was found better to resublime the phthalic anhydride.

The apparatus consisted of a flask which was connected with a reflux condenser and had also an inlet for dry air; the condenser was connected with a U-tube containing calcium chloride and then with two Liebig bulbs containing potassium hydroxide solution. Dry air could thus be drawn through the apparatus, and the hydrogen chloride given off determined. Five grams of phthalic anhydride and 18-20 cc. benzene were placed in the flask and heated until the anhydride was dissolved, after cooling, 9 g. aluminium chloride were added gradually; this was allowed to stand at room temperature for one hour, in order that the hydrogen chloride should not be given off so rapidly as to prevent complete absorption in the Liebig bulbs, and then the flask was heated on the water bath and kept boiling for two hours. 100 cc. of dilute hydrochloric acid (20 cc. conc. hydrochloric acid to 80 cc. water) were added to the cooled contents of the flask, the benzene distilled off with steam, the residue cooled to 0°, and the orthobenzoyl-benzoic acid filtered off; this was washed with cold water, redissolved in sodium carbonate and precipitated with hydrochloric acid. In this way we obtained a 96-97% yield with no phthalic acid and never more than a trace of diphenylphthalide.

When less aluminium chloride was used both phthalic acid and diphenylphthalide were obtained. The diphenylphthalide was separated by its insolubility in sodium carbonate solution and the remaining acids were separated by extracting the benzoyl-benzoic acid from the phthalic acid by chloroform. Small quantities of the two acids were also recovered from the first filtrate containing the aluminium chloride.

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[1] *Ber.*, 41, 3627 (1908).

In the following table the phthalic acid recovered has been omitted and the hydrogen chloride has been expressed in formula weights per formula weight of aluminium chloride used (Al_2Cl_6):

No.	Benzene Cc.	Ph. anhy. Grams.	Al. chl. Grams.	Time boiled. Hours.	Benzoyl-benz. ac. Grams.	Diphen. phth. Grams.	Hydr. chl.
1	18	5	9	2	7.36	None	1.17
2	18	5	9	2	7.29	None	1.18
3	18	5	9	2	7.39	None	1.17
4	18	5	4.5	2	2.03	0.45	1.02
5	18	5	4.5	2	2.01	0.48	0.91
6	18	5	4.5	2	2.47	0.86	1.09
7	18	5	4.5	0.5	2.87	0.17	0.90
8	20	5	4.5	3.5	..	1.17	1.27
9	20	5	4.5	8.5	..	1.36	1.25
10	36	5 + 5	9	2 + 2	5.14	0.88	1.20
11	40	5 + 5	9	2 + 2	6.72	0.96	1.02
12	40	5 + 2	9	2 + 2	7.51	0.30	1.24
13	30	5	18	2	7.23	None	..
14	20	5	4.5 + 4.5	2 + 2	6.50	0.65	1.31
15	20	5	2.3	2	0.78	0.6	1.00

From Nos. 1–3 it will be seen that, using the proportions of the reagents indicated, the yield of orthobenzoyl-benzoic acid is practically constant and the hydrogen chloride given off is nearly 1.2 formula weights per formula weight of aluminium chloride used. There is no diphenylphthalide formed. In Nos. 4–6, using half the amount of aluminium chloride, the yield of orthobenzoyl-benzoic acid is less than one-third and not so constant and diphenylphthalide is found. Nos. 7–9 show that longer boiling materially increases the yield of diphenylphthalide. In Nos. 10–12 the usual proportions of the reagents were used and after two hours' boiling, additional phthalic anhydride was added and boiling continued for two hours. It is known from Nos. 1–3 that these preparations would have yielded no diphenylphthalide at the end of the first two hours' boiling and would have given a 97% yield of orthobenzoyl-benzoic acid, so that the diphenylphthalide obtained must have been due to the action of the additional phthalic anhydride on the intermediate compound. No. 13 shows that increasing the amount of aluminium chloride produces no diphenylphthalide, No. 14 that beginning with a small amount of the aluminium chloride and increasing it during the course of the reaction does not prevent the formation of diphenylphthalide, and in No. 15 only one-quarter of the usual amount of aluminium chloride was used and the yield of orthobenzoyl-benzoic acid was very small.

Since the diphenylphthalide is shown to be produced by the action of the phthalic anhydride on the intermediate product which would have given orthobenzoyl-benzoic acid, experiments were made to see whether other acid anhydrides would have a similar effect.

Expt. 16.—Twenty grams of phthalic anhydride, 80 cc. benzene and 18 g. aluminium chloride, boiled for two hours, then 13.6 g. succinic anhydride added and boiling continued for two hours, gave 11 g. diphenylphthalide and not more than a trace of orthobenzoylbenzoic acid.

Expt. 17.—Fourteen and eight-tenths grams of phthalic anhydride, 80 cc. benzene and 13.3 g. aluminium chloride, boiled for two hours, then 10.2 g. acetic anhydride added and boiling continued for two hours, gave 8.8 g. diphenylphthalide and no orthobenzoyl-benzoic acid.

Von Pechmann[1] found that in the preparation of orthobenzoyl-benzoic acid some diphenylphthalide was found and he also states that diphenylphthalide may be prepared from orthobenzoyl-benzoic acid, aluminium chloride and benzene, but that a better yield was obtained from the mixed anhydride of orthobenzoyl-benzoic and acetic acids.

Expt. 18.—Seven and four-tenths grams of orthobenzoyl-benzoic acid, 20 cc. benzene and 9 g. aluminium chloride were boiled for two hours and gave 0.1 g. diphenylphthalide. This experiment may be compared with Experiment 13, in which an excess of aluminium chloride was used and there must have been present the intermediate compound and aluminium chloride, so that although orthobenzoyl-benzoic acid with aluminium chloride will give a small quantity of diphenylphthalide the intermediate compound with aluminium chloride will give none unless an acid anhydride is present.

Experiments were also made, along the same line, in the preparation of benzophenone from benzoyl chloride, benzene and aluminium chloride. The benzoyl chloride was dissolved in benzene and powdered aluminium chloride added. It is not necessary to add the aluminium chloride gradually when a large excess of benzene is used. The flask was heated very gently on the water-bath for 20–30 minutes and when the evolution of hydrogen chloride became slower the temperature was raised to boiling. Three and one-half hours' boiling was found to give the maximum yield of benzophenone, but the yield of hydrogen chloride was so variable that records are not given. The contents of the flask were poured into 200 cc. of cold water, 10 cc. of conc. hydrochloric acid added and the benzene distilled off with steam. The benzophenone was then extracted with ether, the benzoic acid extracted from the ethereal solution with 10% sodium hydroxide solution and the benzophenone obtained by evaporation of the ether. The benzophenone so obtained was pink in color but was not further purified, as distillation would have involved a considerable and variable loss. Small quantities of benzophenone were also recovered from the distillate containing the benzene.

Expt. 19 (in duplicate).—Twelve and one-tenth grams of benzoyl chloride,

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[1] *Ber.*, 14, 1865 (1881).

130 cc. benzene and 12.1 g. aluminium chloride gave benzophenone: 12.8 g.; 12.8 g.

Expt. 20 (in duplicate).—Twelve and one-tenth grams of benzoyl chloride, 130 cc. benzene and 6.06 g. aluminium chloride gave benzophenone: 5.8 g.; 5.8 g.

Experiments 19 and 20 show that reducing the aluminium chloride to one-half reduces the yield of benzophenone to a little less than one-half. No other product was obtained except benzoic acid.

Expt. 21 (in duplicate).—Twelve and one-tenth grams of benzoyl chloride, 130 cc. benzene and 12.1 g. aluminium chloride, boiled for three and one-half hours, then 8.75 g. phthalyl chloride added and boiling continued for three and one-half hours gave benzophenone: 11.2 g.; 12.1 g.; and diphenylphthalide: 5.1 g.; 4.8 g. This experiment shows that the addition of phthalyl chloride at the end of the preparation for benzophenone gave diphenylphthalide, without materially reducing the yield of benzophenone.

Expt. 22 (in duplicate).—Eight and three-quarters grams of phthalyl chloride, 130 cc. benzene and 6.5 g. aluminium chloride gave diphenylphthalide: 10.0 g.; 10.0 g.

Expt. 23.—Eight and three-quarters grams of phthalyl chloride, 130 cc. benzene and 6.5 g. aluminium chloride boiled for three and one-half hours, then 12.1 g. benzoyl chloride added and boiling continued for three and one-half hours gave diphenylphthalide (not weighed) but no benzophenone.

Expt. 24.—Ten grams of phthalic anhydride, 100 cc. benzene and 12.1 g. aluminium chloride boiled for two hours, then 14 g. phthalyl chloride added and boiling continued for two hours gave diphenylphthalide: 14 g., and no orthobenzoyl-benzoic acid. This shows that phthalyl chloride, added at the end of the preparation for orthobenzoyl-benzoic acid, acts on the intermediate compound in the same way as the acid anhydrides and gives a much better yield of diphenylphthalide.

Expt. 25.—Fourteen grams of phthalyl chloride, 100 cc. benzene and 12.1 g. aluminium chloride boiled for two hours, then 10 g. phthalic anhydride added and boiling continued for two hours gave diphenylphthalide: 19.6 g. In this experiment the addition of phthalic anhydride has somewhat increased the yield of diphenylphthalide (compare Experiment 22).

Expt. 26.—Fourteen and eight-tenths grams of benzoic anhydride, 150 cc. benzene and 20.5 g. aluminium chloride boiled for two hours gave 6.3 g. of benzophenone.

Expt. 27.—Eight and three-tenths grams of phthalic anhydride, 100 cc. benzene and 15 g. aluminium chloride boiled for two hours, then 12 7 g. benzoic anhydride added and boiling continued for two hours, gave 6 g. of benzophenone, and diphenylphthalide and orthobenzoyl-benzoic acid (not weighed). In this experiment it is seen that the benzoic anhydride has the same effect as the other acid anhydrides but gives a considerable yield of benzophenone as well.

Summary.

1. Friedel and Crafts' method of preparing orthobenzoyl-benzoic acid, as used by Heller, was found to give a 97% yield and nearly 1.2 formula weights of hydrogen chloride for each formula weight of aluminium chloride used (Al_2Cl_6).

2. When less aluminium chloride is used the yield of orthobenzoyl-benzoic acid is very much reduced and diphenylphthalide is obtained, and this is found to be due to the action of the phthalic anhydride on the intermediate compound.

3. Succinic anhydride, acetic anhydride, benzoic anhydride and phthalyl chloride also give diphenylphthalide with this intermediate compound.

4. In the preparation of benzophenone from benzoyl chloride, benzene and aluminium chloride, reducing the amount of aluminium chloride reduces the yield almost in the same proportion and the addition of phthalyl chloride gives diphenylphthalide, without materially reducing the yield of benzophenone.

5. Benzophenone may be obtained from benzoic anhydride, benzene and aluminium chloride, but the yield is not good.

6. In the case of the addition of benzoic anhydride to the preparation for orthobenzoyl-benzoic acid, benzophenone is produced in addition to diphenylphthalide.

These experiments were carried out under the direction of F. B. Allan.

UNIVERSITY OF TORONTO

SOME PHYSICAL PROPERTIES OF ETHANE, ETHYLENE AND ACETYLENE.

BY O. MAASS AND D. MCINTOSH

Received February 21, 1914.

In the course of an investigation on the physical properties of bodies at low temperatures, we have found it necessary to measure some of the constants of ethane, ethylene and acetylene, which are not given in the chemical literature. A comparison of these three bodies, each containing two carbon atoms, but with different linkages, is not without interest, while a publication of the results may save labor on the part of some chemists. We give them here, therefore, together with a description of the methods employed in their determination.

Ethane.—The ethane was made from methyl iodide, by the action of the zinc-copper couple. It was washed with alkali, dried by phosphorus pentoxide, passed through three spirals cooled to —78°, twice distilled, the middle portions being retained, and was finally introduced into the density and vapor pressure bulbs. In this method of preparation, the ethane must be repeatedly cooled almost to the point at which it condenses, in order to remove the last traces of methyl iodide.

The vapor pressure and density of the liquid were determined in the apparatus shown in Fig. 1. *B* is a constant temperature bath consisting of a large Dewar flask containing anhydrous ether. *H* is the bulb of a hydrogen thermometer and *D* is a calibrated density bulb with a graduated stem. The bath is cooled with liquid air which is dropped in small portions into *A* and is stirred by a stream of dry air from the tube *C*. S is the apparatus for molecular surface energy determinations; it was used only with acetylene. The bath could be maintained constant within 0.1°.

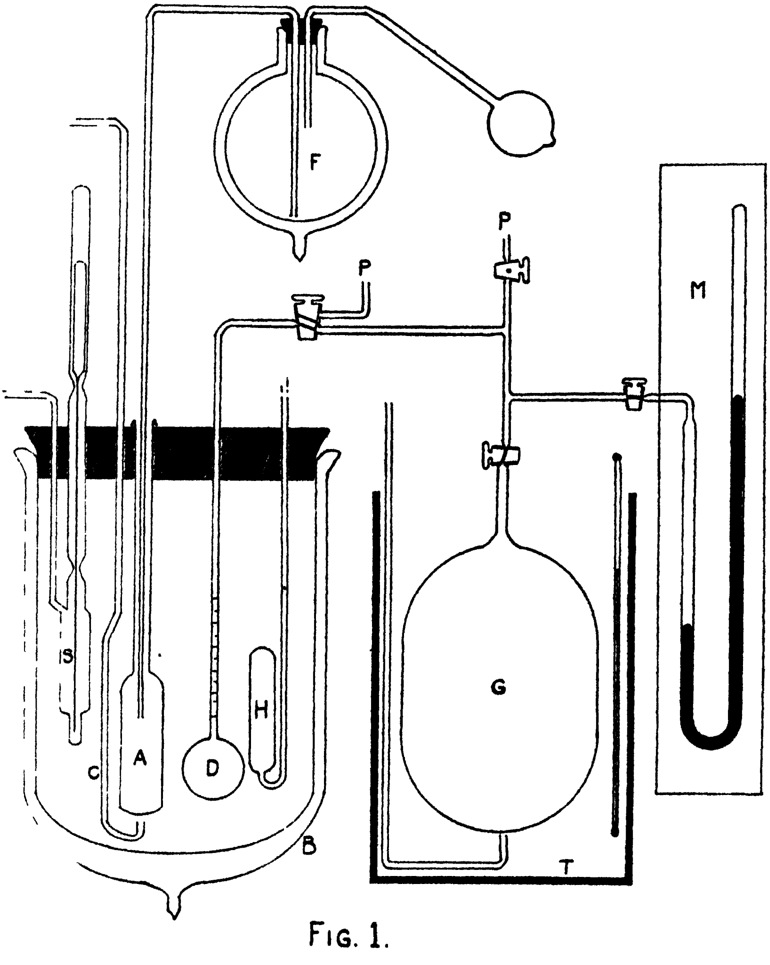

Fig. 1.

The vapor pressures were determined by the manometer *M* connected with the bulb *D*, which was about $^1/_8$ filled with liquid. During the density measurements the bulb was filled to a convenient point on the stem, the variation in volume noted at various temperatures, and the weight found by measuring the gas at a known pressure and temperature in the flask *G*. The volume of *G* was found by weighing it full of water, and that of the various connecting tubes by exhausting the air in them by a Toepler pump and measuring the volume. The apparatus is not drawn to scale.

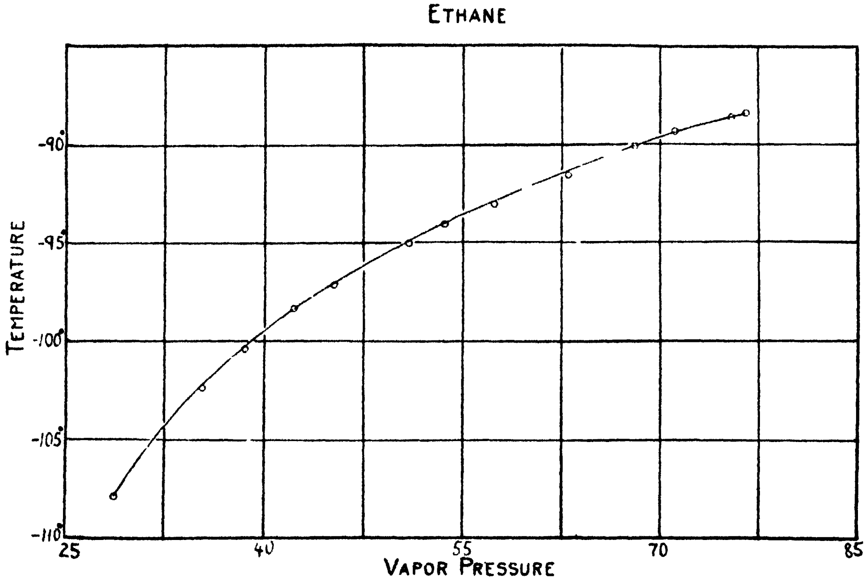

FIG 2.

The result of the vapor pressure experiments are given in Table I and the density determinations in Table II. These are shown as curves in Figs. 2 and 3. The boiling point at normal pressure is —88.5°, the heat of vaporization calculated by the Clausius equation is 14.6 × 10^{10} · ergs for a gram molecule, and the density at the boiling point is 0.5490.

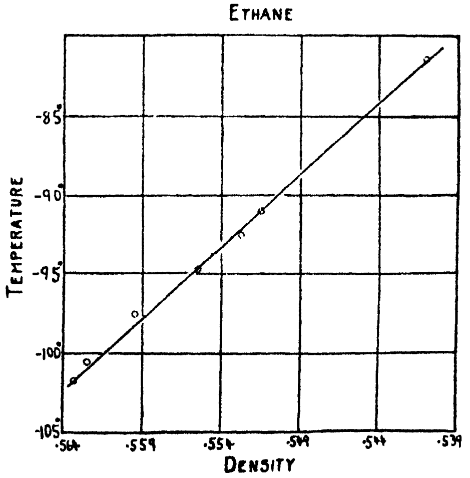

FIG. 3.

TABLE I.

Temperature.	Pressure (mm.).	Temperature.	Pressure (mm.).
—107.9	28.8	93.0	57.5
102.4	35.4	91.5	63.0
...	..	89.9	68.1
100.4	38.5	89.3	71.3
98.2	42.2	88.6	75.4
97.1	45.4	88.4	76.5
95.0	51.0	..	..
94.0	54.6	..	..

TABLE II.

Temperature.	Density.
—101.8°	0.5633
100.6	0.5625
97.6	0.5595
94.8	0.5555
92.6	0.5528
91.1	0.5516
81.7	0.5410

TABLE III.

Temperature.	Density.
—114.2	0.5752
107.7	0.5696
105.9	0.5674
105.0	0.5669
103.3	0.5657
99.4	0.5631

Ethylene.—The vapor pressure of ethylene has been measured by Ramsay and Travers, and the boiling point is given as —102.5°. We have determined, therefore, only the density of the liquid, with the results given in Table III and Fig. 4. The ethylene was made from alcohol by the action of alumina at 450° and was washed, dried and repeatedly distilled as with ethane. Its density, at its boiling point, is 0.5650.

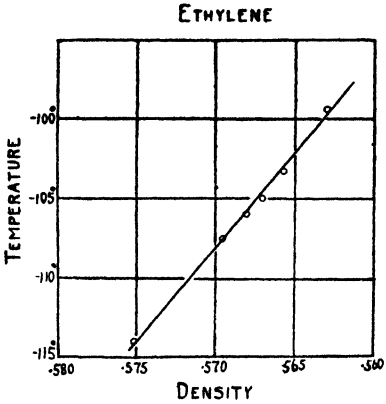

FIG. 4.

Acetylene.—The density and molecular surface energy of this substance were measured at various temperatures. The results of the former agree with the previous determinations of one of us, and need not be given here. The values of the surface energy are shown in Fig. 5 and given in Table IV, where *T* is the

TABLE IV.

Radius of capillary 0.01918 cm.

T.	D.	*h*.	γ.	$\gamma (MV)^{2/3}$.
—77.4°	0.6082	3.160	17.993	220.1
75.7	0.6036	3.135	17.718	217.8
70.5	0.5912	2.960	16.370	204.1
69.0	0.5877	2.915	15.992	200.1
67.0	0.5828	2.870	15.605	196.4
64.0	0.5778	2.780	15.005	189.9
62.4	0.5718	2.705	14.444	184.1

temperature, D the density, h the rise in the capillary tube in centimeters, γ the surface tension in dynes, and $\gamma(Mv)^{2/3}$ the molecular surface energy in ergs.

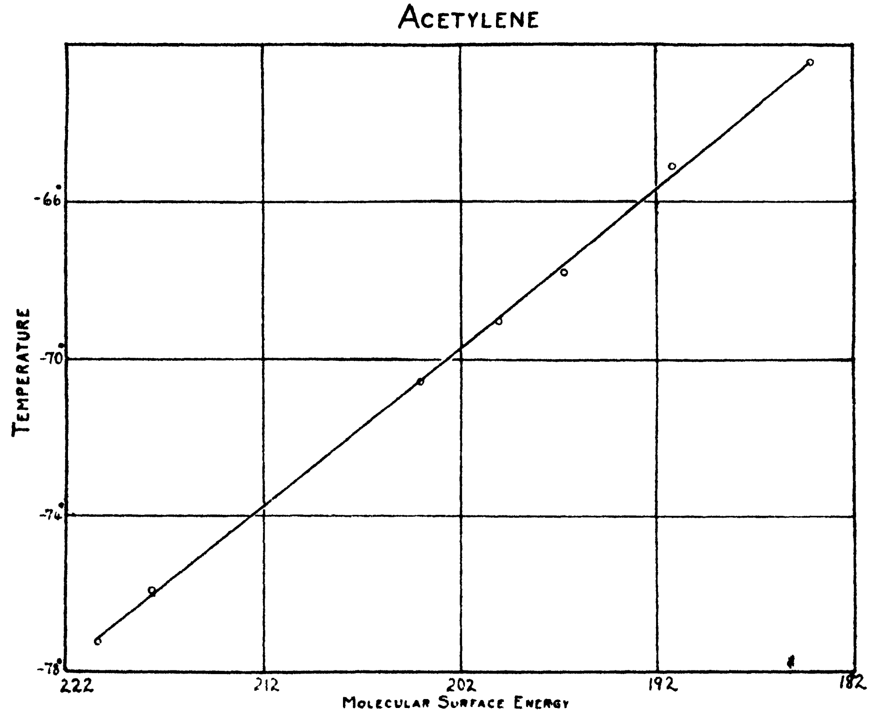

FIG 5

The variation of the molecular surface energy with temperature is 2.40 per degree, a result much higher than that ordinarily found for liquids. Some substances, such as diphenylamine and quinoline, exhibit the same anomaly.

The Atomic Volume of Carbon.—The density of ethane, ethylene and acetylene at their boiling points are 0.5490, 0.565 and 0 618, and their molecular volumes are therefore 54.7, 49.6 and 42.1.

If we take 5.5 as the atomic volume of hydrogen, the atomic volumes of carbon for different linkages are:[1]

Single .	10 9
Double . .	13.8
Triple . .	15.5

In the case of carbon monoxide, its molecular volume is 35.1. When two atoms of chlorine are added, the compound $COCl_2$ has a density of 1.415, at its boiling point, and consequently a molecular volume of 70. Deducting the atomic volumes of C and O, the atomic volume of carbon is seen to be 12.2, in good agreement with Kopp's number. The atomic volume of divalent carbon in the carbon monoxide is 23. It is interesting to note that, if acetylene be assumed to have a divalent and a tetravalent carbon atom, *i. e.*, the acetylidene structure, its atomic volume agrees exactly with that found experimentally.

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[1] See *Bas. Phil. Mag.*, **27**, 355 (1914).

We have endeavored to produce addition compounds of acetylene and hydrobromic at low temperatures. Acetylene is quite soluble in this acid, but solutions containing even 50% of acetylene show no tendency to precipitate compounds at temperatures as low as - 115°.

With liquids having high vapor pressures at their freezing points, such as hydrobromic and hydriodic acid, but particularly with acetylene, the phenomenon of freezing and boiling occurring simultaneously is shown in a striking way. Liquid acetylene in a sealed tube can be supercooled about 5°. As crystallization takes place the remaining liquid boils furiously.

McGill University

[Contribution from the Chemical Laboratory of Washington University.]

THE PREPARATION AND PROPERTIES OF THE NEUTRAL AMMONIUM SALTS OF ORGANIC ACIDS.

By LeRoy McMaster.

Received January 31, 1914

As stated in two previous papers,[1] most of the ammonium salts of organic acids described in the literature are the acid salts instead of the neutral salts Many of the "neutral" salts purchased have also been found to be "acid." This is due to the fact that they have been prepared by neutralizing the aqueous solution of the organic acid with ammonia water or ammonium carbonate and the solution allowed to evaporate to crystallization. The salts thus formed are generally hydrolyzed and the acid salt results. Many of these salts also contain water of crystallization. Neutral ammonium salts free from water of crystallization can be obtained by passing dry ammonia gas into an absolute alcohol or ether solution of the organic acids. Most of the organic ammonium salts are insoluble in alcohol or ether and are thus precipitated. Keiser and McMaster prepared, by this method, the neutral ammonium salts of fumaric, maleic, mesaconic and citraconic acids. I prepared also, by this method, the neutral ammonium salts of propionic, isobutyric, benzoic, cinnamic, malonic, succinic, malic, tartaric, *o*-phthalic and *m*-phthalic acids and studied some of their properties. Many of the properties of the salts made by this method were found to be different

[1] Keiser and McMaster, *Am. Chem. J.*, **49**, 84–87 (1913); *Chem. News*, **108**, 136–137 (1913); McMaster, *Am. Chem. J.*, **49**, 294–301 (1913); *Chem. News*, **108**, 182–183, 193–194 (1913).

from those as described in the literature. This has also been found to be the case with some of the ammonium salts of the organic acids described in this paper.

The work on the preparation and study of the properties of the neutral ammonium salts of organic acids has been continued. They were prepared in both absolute ethyl alcohol and ether. Several were prepared also in methyl alcohol. In several cases the salts were more or less soluble in the alcohols, and, under this condition, they were prepared only in ether. When the experiments were carried out in ethyl alcohol it was generally necessary to keep the flasks surrounded by cold water, for, when the ammonia was passed into the solution, heat was set free due to the action of ammonia on the alcohol and also to the heat of neutralization. Very little, if any, heat was developed when ether was used as the solvent for the acid.

Whenever the ammonium salts are only slightly soluble in ethyl alcohol, they were prepared in this medium rather than in ether, since from an alcoholic solution of the acid they are generally precipitated in a crystalline form. From an ethereal solution they are mostly precipitated in an amorphous state. The neutral ammonium salts were all filtered and washed by suction on alundum crucibles. The organic acids used in this investigation were obtained from Kahlbaum or Schuchardt.

Ammonium Butyrate.—No record can be found of the preparation of this salt other than being mentioned by Pelouze and Gélis[1] as being a deliquescent compound. When dry ammonia gas was run into an ethereal solution of normal butyric acid, a white, granular, crystalline precipitate of neutral ammonium butyrate was formed. The precipitate was quickly filtered by suction on an alundum crucible, washed with ether, and then placed in a vacuum desiccator for a few minutes. The salt is deliquescent and loses ammonia readily on standing in the air. On first dissolving the salt in water, the solution is neutral. The solution soon turns acid, due to hydrolysis. The salt is readily soluble in methyl alcohol, ethyl alcohol and acetic acid, and appreciably so in acetone.

Calc. for $C_4H_7O_2NH_4$: 13.33%; found: 13.31% N.

Ammonium Isovalerianate.—Beilstein states that an acid salt of isovalerianic acid of the formula $NH_4C_5H_9O_2 + 2C_5H_{10}O_2$ is used in medicine. The U. S. Dispensatory describes the commercial valerianic acid as a mixture of two isomeric acids—isovaleric acid and optically active valeric acid. This is true of the valeric acid that is obtained from the *Valeriana officinalis*, the *Angelica archangelica*, and that which results from the oxidation of the amyl alcohol of fermentation with the aid of chromic acid. The "ammonium valerianate" described in the Dispensatory is evidently a mixture of ammonium valerianate and ammonium isovalerianate. It is also acid. Hager[1] states that commercial ammonium valerianate is always the acid salt, as is proved by the acid reaction and the strong rotation of the crystals when placed upon cold water; the neutral salt is obtained only with difficulty, is in prismatic crystals, and is easily liquefied by moderate temperatures. A sample of ammonium valerianate purchased from Kahlbaum was found to be acid. The neutral ammonium salt of isovalerianic acid was prepared by conducting dry ammonia gas into an ethereal solution of the acid. There was formed a snow-white crystalline precipitate which is very deliquescent, and which has an odor like that of the free acid. The salt is very soluble in water. On first dissolving the salt in water, the solution is neutral, but soon becomes acid due to hydrolysis. It is readily soluble in methyl alcohol, ethyl alcohol, acetic acid, and somewhat so in acetone.

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[1] Pelouze and Gélis, *Ann.*, **47**, 249.

Calc. for $C_5H_9O_2NH_4$: 11.76%; found· 11.77% N.

Ammonium Caproate.—No record can be found of the preparation of this salt. Caproic acid, was dissolved in ether, and ammonia passed into the solution. A white precipitate formed which at first was somewhat gelatinous, but soon became crystalline and translucent. The salt is very deliquescent and has to be filtered and washed very quickly by suction. When dissolved in water a neutral solution is formed, which soon becomes acid. The salt is very soluble in methyl alcohol, ethyl alcohol and acetic acid. On standing in the air, it readily loses ammonia. Analysis proved it to be the neutral ammonium caproate.

Calc. for $C_6H_{11}O_2NH_4$· 10.52%; found: 10.53% N.

Ammonium Crotonate.—On passing ammonia gas into a saturated alcoholic solution of crotonic acid, a beautiful glistening white precipitate formed. The precipitate was quickly filtered, washed with ether and dried for a short time in a vacuum desiccator. The ammonium salt was also prepared in ether When ammonia gas was passed into an ethereal solution of the acid, there was first formed a very gelatinous precipitate which soon became an amorphous powder. The salt prepared in either medium is not hygroscopic, but is very soluble in water. The aqueous solution is neutral, but soon hydrolyzes. The neutral ammonium salt, both crystalline and amorphous, has the odor characteristic of crotonic acid. It is readily soluble in methyl alcohol, ethyl alcohol and acetic acid, but insoluble in ether and chloroform.

Prepared in alcohol· Calc. for $C_4H_5O_2NH_4$: 13.60%; found: 13.61% N.
Prepared in ether Found: 13.60% N.

Although many of the salts of crotonic acid have been prepared and studied, no mention of the neutral ammonium salt can be found.

The Ammonium Salt of Ethyl Malonic Acid.—When ammonia gas was run into an alcoholic or an ethereal solution of ethyl malonic acid, there was first formed a white precipitate which is somewhat mucilaginous. This precipitate, after a short time, changed to a semi-crystalline one, when prepared in alcohol, and to an amorphous powder when prepared in ether. The salt prepared by either method is somewhat hygroscopic, and loses ammonia readily in moist air. The salt was filtered by suction, washed with ether, and dried in a desiccator. When dry the salt has the appearance of dry paper pulp. The aqueous solution was neutral to sensitive litmus paper. It is slightly soluble in ethyl alcohol, readily soluble in methyl alcohol and acetic acid, but insoluble in acetone. A solution of the salt is not precipitated by ferric chloride. No mention of this salt is made in the literature.

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[1] U. S. Dispensatory, 18th edition, p. 463. *Pharm. Centralb.*, 1879, p. 465.

Prepared in alcohol Calc for $C_5H_6O_4(NH_4)_2$ 16.86%, found 16.87% N
Prepared in ether Found 16.87% N

Ammonium Glutarate.—When ammonia is passed into an alcoholic solution of glutaric acid there is formed a white amorphous precipitate, which soon becomes crystalline and granular in appearance. This salt can also be prepared in ether. The salt thus formed is the neutral ammonium glutarate, soluble in water, methyl alcohol and acetic acid. It is insoluble in ether. The salt is not deliquescent.

Calc. for $C_5H_8O_4(NH_4)_2$ 16.86%, found 16.85% N

Ammonium Adipate.—This salt has been prepared by Dieterle and Hell[1] by treating an aqueous solution of adipic acid with an excess of ammonia water and evaporating the mixture to crystallization. Small, glittering leaflets were formed. Larger crystals of the neutral salt were obtained by allowing the aqueous solution to evaporate spontaneously in an atmosphere of ammonia. The salt is described as being stable in the air. It loses one molecule of ammonia when dried at 100°, forming the acid salt. Upon heating the salt to 120-150°, all of the ammonia is driven off and the free adipic acid is formed. This salt has also been described by Arppe[2] as forming monoclinic crystals.

Ammonia was passed into an alcoholic solution of adipic acid and a white crystalline salt was formed. It was filtered, washed with alcohol and ether and dried in a desiccator. The salt is stable in the air and an aqueous solution of it is neutral. It is slightly soluble in ethyl alcohol and insoluble in ether. It is appreciably soluble in methyl alcohol, from which it crystallizes in small, beautiful leaflets. Determination of the nitrogen proved it to have the composition of the neutral salt.

Calc. for $C_6H_8O_4(NH_4)_2$: 15.55%; found 15.50% N

Ammonium Pimelate.—This salt would not precipitate when ammonia gas was run into an alcoholic solution of pimelic acid, due to its solubility in alcohol. When ammonia gas was passed into an ethereal solution of the acid a white, gummy precipitate was formed which would not crystallize. Ammonia was then passed into a solution of the acid dissolved in alcohol and ether. A fine, white powder was formed which was filtered, washed with ether and dried in a desiccator. This salt gave a neutral solution when dissolved in water, in which it is very soluble. It is not hygroscopic, but loses ammonia very readily in both dry and moist air, passing to the acid salt. It is quite soluble in methyl alcohol and acetic acid. It crystallizes from ethyl alcohol in leaflets. Analysis showed it to be the neutral ammonium pimelate.

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[1] Dieterle and Hell, *Ber.*, 17, 2221 (1884).

[2] Arppe, *Z. Chem.*, p. 301 (1865).

Calc. for $C_7H_{10}O_4(NH_4)_2$: 14.43%; found: 14 40% N.

Ammonium Sebate.—Neison[1] states that the ammonium salts of sebacic acid can be obtained in solution, but they are invariably partially decomposed, with loss of ammonia, on attempting to obtain them in the solid state, whether the evaporation is conducted *in vacuo*, at the heat of a water bath, over sulfuric acid, or spontaneously in a current of dry air.

The neutral ammonium salt of this acid was prepared in a *solid state* by the usual method in both alcohol and in ether. When precipitation takes place in alcohol, there is first formed a slightly gelatinous precipitate which changes to a white, crystalline powder. When prepared in ether the white powder is not crystalline. The precipitate in each case was filtered, washed with ether and dried for a short time over sulfuric acid in a vacuum desiccator. The salt is readily soluble in water to which it imparts a neutral reaction. The salt was still neutral to litmus after standing for one month in a tightly stoppered bottle. It is not deliquescent but loses ammonia in moist air. It is slightly soluble in ethyl alcohol. The salt crystallizes from methyl alcohol in small crystalline flakes.

Analysis of the salt prepared in alcohol showed it to be the neutral ammonium salt of sebacic acid.

Calc. for $C_{10}H_{16}O_4(NH_4)_2$: 11.86%; found: 11.86% N.

Ammonium Tartronate.—Petriew[2] describes this salt as needles which decompose at 100°. Tartronic acid was dried at 100°, at which temperature it loses its water of crystallization, dissolved in alcohol and ammonia conducted into the solution. A fine, glistening, white, crystalline precipitate formed. This salt was filtered, washed with ether and dried in a desiccator. It is not deliquescent and an aqueous solution of it is neutral to different indicators. It is insoluble in methyl alcohol and ether. When treated with acetic acid, free tartronic acid is formed.

Calc for $C_3H_2O_5(NH_4)_2$: 18.18%; found· 18.17% N.

Ammonium Racemate.—Racemic acid was dried at 100°, and ammonia passed into an alcoholic solution of it. A white precipitate, somewhat flocculent at first, was formed. This changed to a crystalline powder, which as soon as neutral, was filtered and washed with alcohol and ether. An aqueous solution of the salt was neutral towards different indicators. The salt is not deliquescent. It is insoluble in methyl alcohol, ethyl alcohol and ether.

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[1] Neison, *J. Chem. Soc.*, **27**, 301.

[2] Petriew, *J. Russ Chem Soc* , **10**, 152.

Calc for $C_4H_4O_6(NH_4)_2$ 15 21%, found: 15.21% N

Ammonium Itaconate.—Baup[1] states that, like many other ammonium salts, neutral ammonium itaconate does not crystallize since on evaporation or standing in the air it loses ammonia and the acid salt forms.

When ammonia gas is passed into an alcoholic solution of itaconic acid, until a portion of the salt on being dissolved in water shows a neutral solution, there is formed a white, granular, crystalline precipitate of neutral ammonium itaconate. When the ammonia is first passed in, the precipitate formed is slightly gelatinous. The salt was washed with alcohol and ether, and dried for a short time over sulfuric acid in a vacuum desiccator. It is very hygroscopic. In dry air the salt is stable, but loses ammonia in moist air. It is soluble in acetic acid, but insoluble in methyl alcohol, ethyl alcohol and acetone.

The neutral ammonium salt of itaconic acid can also be precipitated in ether as an amorphous compound. The salt prepared in either alcohol or ether readily hydrolyzes when dissolved in water.

Prepared in alcohol Calc for $C_5H_4O_4(NH_4)_2$ 17 07%; found. 17 07% N
Prepared in ether Found 17 07% N

Action of Ammonia on some other Organic Acids.—Attempts to prepare the neutral ammonium salts of isosuccinic, pyrotartaric, aconitic and several other acids have so far given unfavorable results. The precipitates formed were usually very mucilaginous and would not crystallize, even if the ammonia was conducted into the alcoholic or ethereal solution for a long time. Methyl alcohol was tried as a medium in which to precipitate these salts but without success. Work on these acids is being continued. A number of neutral ammonium salts of the higher fatty acids and of the aromatic series have been prepared and analyzed. The results will be given in a future paper. This investigation is being continued with other organic acids.

ST LOUIS, MO.

THE DOUBLE AURIC IODIDES OF SUBSTITUTED AMMONIUM BASES.

BY SATYARANJAN DAS GUPTA

Received February 2, 1914.

The application of the method of double decomposition in the formation of double salts is being systematically studied by Datta and already some interesting results have been obtained by him. Though there are a few scattered instances of salt formation by the incidental application of this method, yet this has been clearly expounded by him as a principle susceptible of much wide application. He prepared a series of double iodides of platinum and cupric copper by starting with a solution of platinic and cupric chlorides.[1] Later on, he prepared a few more of the double platini-iodides by precisely the same method.[2] The double iodides of cadmium and mercury with the substituted ammonium bases have also been prepared by him as an extension of his method.[3] The same principle has been applied by him in the preparation of double carbonates of the alkaline earth metals and lead with potassium carbonate, which cannot be prepared by direct means.

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[1] Baup, *Ann.*, 19, 29.

These facts induced me to investigate the double auric iodides by the method applied by Datta, *viz.*, the addition of a soluble salt of gold (preferably the chloride) to various substituted ammonium iodides. Now Johnston[4] prepared several auric iodides with the alkali metals and ammonium by adding auric chloride to the alkali iodide and then allowing the solution which contains the double salt to crystallize. They have also been prepared by him by allowing the solution of auric iodide in alkali iodide to crystallize. Now by the indirect method of Datta the preparation of the double salts with alkali metals has been found to fail, owing to the great solubility of the double salts. The double auric iodide of caesium can, however, be precipitated directly by adding auric chloride to caesium iodide solution, owing to its comparatively small solubility. The double auric iodides of the substituted ammonium bases can be precipitated directly by adding a solution of auric chloride to the solutions of iodides of bases. But the reaction has been found to fail with ethylammonium, diethylammonium, isobutylammonium, allylammonium and anilinium iodides.

The following double iodides have been prepared:

Caesium Auric Iodide, $CsI.AuI_3$.—On adding a solution of auric chloride to a solution of caesium iodide, a black precipitate came down which was shaken with the mother liquor for some time. It was filtered and dried in the steam oven. The compound is of a black shining crystalline form.

Analysis: 0.1436 g. gave 0.1603 AgI; I = 60.33% Calc. for $CsI.AuI_3$, 60.69%

Methylammonium Auric Iodide, $CH_3H_2HI.AuI_3$.—Methylaminehydroiodide is prepared by adding methylamine to hydriodic acid till the faint brown color is turned colorless. It is evaporated to dryness on the water bath, when a white crystalline powder was obtained. This was dissolved in water to form a moderately strong solution and then a fairly strong solution of auric chloride was added, when a black precipitate was formed, leaving the supernatant liquid dark brown, showing that the salt formed is moderately soluble in water. This was then washed with a small quantity of water on the filter paper and then allowed to dry in a desiccator.

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[1] Datta, *J. Chem. Soc.*, **103**, 426 (1913).

[2] THIS JOURNAL, **35**, 1185 (1913).

[3] *Ibid.*, **35**, 949 (1913).

[4] *Phil. Mag.*, **9**, 266 (1836).

Analysis 0.1030 g gave 0.0278 g Au = 26.83% 0.0690 g gave 0.0877 g AgI; I = 68.70% Calc for CH_3NH_2HI AuI_3 Au = 26.76%, I = 68.90%

The compound is of a dark black, shining, crystalline form. It changes its color from black to yellowish brown on long standing, proving that the compound decomposes slowly with the formation of aurous iodide and evolution of iodide.

Butylammonium Auric Iodide, $C_4H_9NH_2HI.AuI_3$.—A solution of auric chloride is added to a solution of butylamine hydroiodide, when a fine black crystalline precipitate comes down immediately. The solution of auric chloride is added gradually, and during each addition the solution is vigorously agitated. The precipitate is then filtered and washed with a little water. The salt is slightly soluble in water and its solution gives a pale red color.

0.1093 g gave 0.0298 g Au, Au = 25.43%, calc for $C_4H_9NH_2HI$ AuI_3; Au = 25.28%

Dipropylammonium Auric Iodide, $3N(C_3H_7)_2H_2I.AuI_3$.—On adding a strong solution of auric chloride to a solution of dipropylammonium hydroiodide, a tarry, brown, oily, liquid is obtained which suffers no change even on keeping it for some days with the mother liquor. It was then suspected that the double salt itself might be liquid. The mother liquor was decanted off from the oil and the oil was then washed several times with water. The tarry oil was dried and the gold estimated by ignition. The tarry oil on standing in the vacuum desiccator over sulfuric acid for several days, however, solidified to a black, pasty mass.

0.1984 g gave 0.0308 g Au Au = 15.52%, calc for $3CN(C_3H_7)_2H_2I$ AuI_3, Au = 16.10%

Tripropylammonium Auric Iodide, $4N(C_3H_7)_3HI.AuI_3$.—The substance was of a pasty and somewhat liquid consistency and was prepared in exactly the same manner as the dipropylammonium auric iodide The tarry liquid appeared brown in thin layers.

0.4723 g gave 0.0584 g Au, Au = 12.35%, calc for $4N(C_3H_7)_3HI$ AuI_3; Au = 11.85%

Tetramethylammonium Auric Iodide, $4N(CH_3)_4I.3AuI_3$- This was prepared according to precisely the same method by adding a solution of auric chloride to a moderately dilute solution of tetramethylammonium iodide, when at first a brownish black precipitate is formed, which turns black on shaking. It was washed and dried as usual The salt is sparingly soluble in water.

0.1006 g. gave 0.0231 g. Au; Au = 22.96%; calc. for $4N(CH_3)_4I.3AuI_3$; Au = 23.38%.

Tetraethylammonium Auric Iodide, $4N(C_2H_5)_4I.3AuI_3$.—To a saturated solution of tetraethylammonium iodide a solution of auric chloride is added drop by drop when a blackish brown precipitate first appears which changes to black on keeping for some time and shaking. It is then filtered, washed and allowed to dry.

0.1257 g. gave 0.0269 g. Au; Au = 21.40%; calc. for $4N(C_2H_5)_4I.3AuI_3$; Au = 21.39%.

Quinolium Auric Iodide, $2C_9H_7NHI.AuI_3$.—When quinoliumhydroiodide is dissolved in a moderate quantity of water, a brown, clear solution is formed, but on attempting to dilute it with water it becomes hazy like an emulsion. This may be due to dissociation, on dilution, into quinoline and hydroiodic acid.

To a clear solution obtained in the above manner a dilute solution of auric chloride is added drop by drop with constant shaking. At first a hazy, oily, emulsion of dirty brown color is produced which, on further agitation and addition of auric chloride, becomes crystalline and falls to the bottom, leaving the supernatural liquid only faintly yellow. The compound on filtration appeared of a fine crystalline appearance and is of a black color. The salt is slightly soluble in water to form a pale yellow solution.

0.1558 g. gave 0.0282 g. Au; Au = 18.10%; 0.0992 g. gave 0.1058 g. AgI; I = 57.66%; calculated for $2C_9H_7NHI.AuI_3$; Au = 18.04; I = 58.15%.

Quinolineethylammonium Auric Iodide, $4C_{11}H_{12}NI.3AuI_3$.—To a saturated solution of quinoline ethyliodide, a moderately dilute solution of auric chloride is added drop by drop when a black precipitate comes down immediately which was filtered and washed as usual. The salt was perfectly black and was of granular character.

0.1204 g. gave 0.0254 g. Au; Au = 21.09%; calc. for $4C_{11}H_{12}NI.3AuI_3$; Au; Au = 20.56%.

Pyridinium Auric Iodide, $4C_5H_5NHI.3AuI_3$.—To a strong solution of pyridinium hydroiodide, a dilute solution of auric chloride is added, when at first a blackish precipitate is produced which disappears again and produces a haziness but on continual shaking it is gradually transformed into a black precipitate which soon collects at the bottom. The supernatant liquid was colored yellowish brown.

0.1406 g. gave 0.0332 g. Au; Au = 23.54%; calc. for $4C_5H_5NHI.3AuI_3$; Au = 23.07%.

During the preparation of these double salts, vigorous and constant shaking is necessary during each addition of the solution of auric chloride, in order to ensure the completion of the double decomposition—as otherwise secondary products may be formed. Moreover, it had been observed, in some cases, that according to different conditions of carrying out the preparation different types of salts were obtained. Sometimes a salt of constant composition was not obtained but what was in all probability a mixture of the different types.

I take this opportunity to express my best thanks to Prof. Rây for his encouragement in carrying out the above investigation.

PRESIDENCY COLLEGE, CALCUTTA.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

TRICRESOL AS A SUBSTITUTE FOR TOLUENE IN ENZYME WORK.[1]

BY SARA S. GRAVES AND PHILIP ADOLPH KOBER

Received January 12, 1914.

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1. Introduction. 2. Experimental: Action of tricresol on: (*a*) Trypsin; (*b*) Erepsin; (*c*) Pepsin, (*d*) Lipase, (*e*) Urease, (*f*) Diastase; (*g*) Invertase. 3. Summary.

1. Introduction.

The results of many enzyme experiments are probably worthless because sterile conditions were not maintained by means of a suitable preservative. To overcome this difficulty before beginning a study of the digestive ferments, it was desirable to find a substitute for toluene, the preservative now in general use.

Toluene has several distinct disadvantages: (1) It evaporates readily, the boiling point being 110° to 112°. (2) It often produces a cloudiness which interferes with optical methods, because of its low solubility in water. (3) It clings to the glass in oily drops, introducing errors in volumetric measurement and necessitating the use of a clean pipet each time. (4) Its bactericidal power is uncertain. The deterioration of a casein solution, after standing at room temperature several months, suggested that toluene does not prevent bacterial action, an idea which has been strengthened by a recent article of Benians on "The Resistance of Various Bacteria to the Disinfecting Action of Toluol and the Allied Bodies, Benzol and Xylol."[2]

After trying formaldehyde, which, in strong solutions, caused decoloration with proteins and in weak solutions was ineffective, as were sodium chloride and boric acid, a saturated solution of tricresol was found in the laboratory. According to E. J. Banzhaf,[3] who suggested the use of tricresol in this connection, the late Dr. A. H. Koelker, while working in this laboratory, had determined that a 0.1% tricresol solution did not interfere with the action of proteases, using the optical method with peptides as developed by Abderhalden and Koelker. No claim, therefore, is made as to the priority of this idea, but it is believed that no results have heretofore been published on this point.[1]

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[1] Read before the American Society of Biological Chemists, Philadelphia Meeting, Dec., 1913.

[2] T. H. C. Benians, *Z. Chemotherap.*, 1, 28 (1913).

[3] Private communication.

Tricresol is so well known as a disinfectant that the statement of bacteriologists has been accepted that it is much more powerful germicide than toluene and that 0.1% solution is sufficient to prevent bacterial growth. It is the object of this paper to show that in physical and chemical properties it is more suitable than toluene and that it has little or no injurious effect upon the enzymes.

Tricresol has the following advantages: (1) It is practically non-volatile, the boiling point being 190°. (2) It is soluble in water to the extent of 2%, causing no cloudiness. (3) It runs clean from a pipet.

2. Experimental.

To show the effect of tricresol on the enzymes, a number of experiments have been performed on proteases, (trypsin, erepsin and pepsin) on lipases, a urease, diastases, and on an invertase, using toluene as a standard.

It has been found convenient to use a saturated solution, pipetting off the supernatant liquid. In working with enzymes and proteins, where slight alkalinity or acidity interferes with the action or precipitation, the slightly acid solution was neutralized with $N/10$ sodium hydroxide. One or two series, as examples of each enzyme, will serve to illustrate the procedure and make clear the results.

(*a*) *Trypsin.*[2]—The activity of each of the three proteases, trypsin, erepsin and pepsin was determined by its power to digest protein according to the nephelometric method of Kober.[3]

EXPERIMENT I.

Solutions I.

(*a*) 0.1 g. trypsin in 100 cc. of 0.2% tricresol, allowed to stand at room temperature for 24 hours.

(*b*) 0.1 g. trypsin in 100 cc. of water, and 2 cc. toluene, allowed to stand at room temperature for 24 hours.

Solutions II.

(*a*) 10 cc. of 0.01% trypsin made from solution I*a*, 25 cc. of 0.1% "sodium caseinate" solution[4] 3 cc. 2% tricresol, and made up to 100 cc. with water.

(*b*) 10 cc. of 0.01% trypsin, made from solution I*b*, 25 cc. 0.1% "sodium caseinate" solution, made up to 100 cc. with water to which was added 2 cc. of toluene.

Solutions III.

(*a*) 5 cc. of solution II*a*, 10 cc. of water and 15 cc. of 3% sulfosalicylic acid.

(*b*) 5 cc. of solution II*b*, 10 cc. water and 15 cc. of 3% sulfosalicylic acid.

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[1] Koelker, in the last work which he published, used toluene.

[2] Fairchild's "Trypsin."

[3] *J. Biol. Chem.*, 13, 485 (1913); THIS JOURNAL, 35, 290, 1586 (1913).

[4] The "sodium caseinate" solutions used in this work were made by dissolving 0.1 g. of casein with 1 cc. of $N/10$ sodium hydroxide and diluting with water.

Solutions III were taken at intervals and nephelometric readings made in comparison with a standard solution containing 5 cc. 0.01% casein solution, 10 cc. of water and 15 cc. of 3% sulfosalicylic acid.

TABLE I.

Preservative.	Time of action. Hrs.	Standard. Mm.	Control. Mm.	15 min. Mm.	30 min. Mm.	60 min. Mm.
Tricresol, 0.2%...	24	15.0	8.0	12.7	22.5	off scale (about 35)
Toluene...... ..	24	15.0	7.9	11.2	15.5	off scale (about 35)

EXPERIMENT II.

0.5% tricresol solution—other directions were followed as in the preceding experiment.

TABLE II.

Preservative.	Time of action Hrs.	Standard. Mm.	Control. Mm.	15 min Mm.	30 min. Mm.	60 min. Mm.	120 min. Mm.
Tricresol, 0.5%...	48	15	6.6	8.2	11.0	16.6	off scale
Toluene.	48	15	6.7	8.0	10.8	12.1	off scale
Tricresol, 0.5% .	72	15	6.7	8.2	10.9	11.9	off scale
Toluene...	72	15	7.0	8.0	9.3	11.2	off scale

From the above data it seems that trypsin is not affected by 0.5% tricresol.

(*b*) *Erepsin.*[1]—

EXPERIMENT I.

Solutions I.

(*a*) 0.1 g. of erepsin in 100 cc. of 0.2% tricresol, allowed to stand at room temperature for 24 hours.

(*b*) 0.1 g. of erepsin in 100 cc. of water and 2 cc. of toluene, allowed to stand at room temperature for 24 hours.

Solutions II.

(*a*) 5 cc. of solution I*a*, 5 cc. *N*/10 HCl, 25 cc. 0.1% casein, 3 cc. 2% tricresol, made up to 100 cc. with water.

(*b*) 5 cc. of solution I*b*, 5 cc. *N*/10 HCl, 25 cc. 0.1% casein, 2 cc. of toluene, made up to 100 cc. with water.

Solutions III.

(*a*) 5 cc. of solution II*a*, 10 cc. of water and 15 cc. of 3% sulfosalicylic acid

(*b*) 5 cc. of solution II*b*, 10 cc. of water and 15 cc. of 3% sulfosalicylic acid

TABLE III.

Preservative.	Time of action. Hrs.	Standard. Mm.	Control. Mm.	15 min. Mm.	30 min. Mm.	60 min. Mm.	3½ hrs. Mm
Tricresol, 0.2%...	24	15	4.8	6.7	7.7	13.1	off scale
Toluene..........	24	15	4.8	5.8	6.5	10.6	off scale

EXPERIMENT II.

0.5% tricresol in solution I*a*, and 10 cc. 0.1% erepsin in solution II*a* and II*b*, were the changes made for this experiment.

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[1] Johnson and Johnson's Papoid.

TABLE IV.

Preservative.	Time of action. Hrs.	Standard. Mm.	Control. Mm.	15 min. Mm.	30 min. Mm.	60 min. Mm.
Tricresol, 0.5%	24	15	7.1	11.7	17.9	31.5
Toluene	24	15	7.2	11.9	19.6	33.0
Tricresol, 0.5%	48	15	10.7	17.4	23.8	off scale
Toluene	48	15	11.0	21.9	35.0	off scale

The above results show that erepsin does not seem to be affected by 0.2% tricresol during the usual time of incubation (24 hrs.) but the activity is slightly retarded by 0.5% solution in 24 hrs. and that the inhibitory action is more evident on long standing.

(*c*) *Pepsin.*[1]—

EXPERIMENT I.

Solutions I.

(*a*) 0.1 g. of pepsin in 100 cc. of 0.2% tricresol allowed to stand at room temperature for 24 hours.

(*b*) 0.1 g. of pepsin in 100 cc. of water and 2 cc. of toluene allowed to stand at room temperature for 24 hours.

Solutions II.

(*a*) 10 cc. of 0.01% pepsin made from solution I*a*, 25 cc. of 0.1% edestin[2] solution (acid), 3 cc. 0.2% tricresol made up to 100 cc. with water.

(*b*) 10 cc. of 0.01% pepsin made from solution I*b*, 25 cc. 0.1% edestin solution (acid) made up to 100 cc. with water and 2 cc. of toluene added.

Solutions III.

(*a*) 5 cc. of solution II*a*, 10 cc. of water, 15 cc. NaCl solution 1-3.

(*b*) 5 cc. of solution II*b*, 10 cc. of water, 15 cc. NaCl solution 1-3.

Solutions III were compared with a standard solution containing 5 cc. of 0.01% edestin, 10 cc. of water and 15 cc. NaCl solution.

TABLE V.

Preservative.	Time of action. Hrs.	Standard. Mm.	Control. Mm.	15 min. Mm.	30 min. Mm.	60 min. Mm.
Tricresol, 0.2%	24	15	8.0	11.5	27.4	off scale
Toluene	24	15	8.5	11.4	27.4	off scale

EXPERIMENT II.

0.5% tricresol solution in solution I*a* was the only change made for this experiment.

TABLE VI.

Preservative.	Time of action. Hrs.	Standard. Mm.	Control. Mm.	15 min. Mm.	30 min Mm.
Tricresol, 0.5%	24	15	10.2	15.3	off scale
Toluene	24	15	10.9	16.4	off scale
Tricresol, 0.5%	48	15	10.7	16.4	off scale
Toluene	48	15	10.9	16.7	off scale
Tricresol, 0.5%	72	15	9.0	13.1	26.6
Toluene	72	15	8.6	15.3	off scale

---

[1] Parke, Davis & Co., Pepsin (scales).

[2] The edestin solutions used in this work were made by dissolving 0.1 g. of edestin in 3 cc. of $N/10$ hydrochloric acid and diluting with water.

From the above results it seems that pepsin is not affected by 0.5% tricresol in 48 hours, though the action seems to be slightly retarded in 72 hours.

(*d*) *Lipase.*—The activity of lipase was determined by its power to hydrolyze ethyl butyrate and triacetin according to the suggestions of K. G. Falk.[1] The results given cc. *N*/10 acid produced in 24 hours at 38–40° are means of duplicate experiments and are corrected for blanks. 0.2 g. of castor bean lipase, 1 cc. of ethyl butyrate or 1/2 cc. triacetin, 5 cc. 1% tricresol or 0.5 to 1 cc. toluene made up to 25 cc. with water.

TABLE VII.

Substance.	Ester.	Toluene. Cc. *N*/10 acid.	0.2% tricresol Cc. *N*/10 acid
C. B. L. (*a*), 0.2 g.	Ethyl butyrate	1.43	1.20
	Ethyl butyrate	1.47	1.18
C. B. L. (*b*), 0.2 g.	Triacetin	2.00	1.70

EXPERIMENT II

Pancreatin as specified, otherwise the directions are as given in the preceding experiments.

TABLE VIII

Pancreatin.	Ester.	Toluene Cc. *N*/10 acid.	0.2% Tricresol. Cc. *N*/10 acid.
0.1 g.	Ethyl butyrate	3.21	5.17
	Triacetin	4.63	2.28
0.05 g.	Ethyl butyrate	2.29	2.63
	Triacetin	2.85	1.20

The results of these preliminary experiments were kindly obtained by K. G. Falk in connection with his work on lipase. The action of castor bean lipase seems to be retarded by tricresol, but with pancreatin and ethyl butyrate, the action seems to be accelerated while with pancreatin and triacetin, the action seems to be retarded.

The average of 10 experiments each, made later by ourselves, substantiate Falk's results: 0.1 g. of pancreatin was used with varying amounts of tricresol as specified; otherwise, the directions were the same as in the preceding experiments.

TABLE IX.

Ester.	0.2% tricresol.	Toluene.	0.1% tricresol	Toluene.
Ethyl butyrate..........	4.37	3.93	4.58	4.22
Triacetin..........	2.08	3.45	2.64	3.75

(*e*) *Urease.*—The activity of urease was determined by the action of the extract of powdered soy bean on urea, according to the methods of E. K. Marshall, Jr.[2] The results are expressed as cc. of *N*/10 acid necessary to neutralize the ammonia produced in 18 hours at 38–40°.

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[1] THIS JOURNAL, **35**, 211 (1913).

[2] *J. Biol. Chem.*, **15**, 487 (1913); **14**, 283 (1913).

EXPERIMENT I.

(*a*) 45 cc. of soy bean extract, 5 cc. of 2% tricresol, were allowed to stand 24 hours at room temperature.

(*b*) 45 cc. of soy bean extract, 5 cc. of water and 2 cc. of toluene, were allowed to stand 24 hours at room temperature.

0.025 g. of urea, 5 cc. of water and 5 cc. of extract "*a*" or "*b*" were allowed to stand in a tightly stoppered test tube at 38–40° for 18 hours. 5 cc. saturated solution of sodium carbonate were then added and the ammonia distilled according to Folin's micro-method.[1]

TABLE X.

0.2% tricresol. Cc. of *N*/10 acid.	Toluene. Cc. of *N*/10 acid.
6 92	6.72
7.28	7.07
7.68	7.03
6.87	6 25
6 98	6 10
Average, 7 14	Average, 6.63

(*a*) 12.5 cc. 2% tricresol and 37.5 cc. of soy bean extract, allowed to stand for 48 hours at room temperature.

(*b*) 12.5 cc. of water, 37.5 cc. of soy bean extract and 2 cc of toluene, allowed to stand for 48 hours at room temperature.

0.025 g. of urea, 5 cc. of extract (*a*) or (*b*) and 25 cc. of water were allowed to stand in a tightly stoppered flask at 38–40° for 18 hours. The ammonia was then titrated directly with *N*/10 acid, using methyl orange as indicator, according to Marshall's clincial method.

TABLE XI.

0.5% tricresol. Cc. *N*/10 acid.	Toluene. Cc. *N*/10 acid.
8.24	7.95
7.80	7 95
7.70	7 73
7 80	7.73
Average, 7.88	Average, 7.84

The results of experiments 1 and 2, indicate that the action of urease is not hindered by 0.5% tricresol solution during 48 hours.

(*f*) *Diastase.*—The activity of diastase was determined by the time required to digest a given amount of starch, testing with iodine[2] for the disappearance of starch-iodine color.

EXPERIMENT[3]

Taka diastase.

(*a*) 0.05 g. of taka diastase, 5 cc. of 1% tricresol and 5 cc. water.

(*b*) 0.05 g. of taka diastase, 10 cc. of water and 1 cc. of toluene.

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[1] *J. Biol. Chem.*, 11, 501 (1912).

[2] Tricresol decolorizes the iodine somewhat, so that in each test an excess of iodine was added before the color was noted.

[3] Parke, Davis & Co., Taka diastase.

After standing 24 hours, 50 cc. of 2% starch solution were added to each diast[illegible] solution, and at intervals portions were taken out diluted with wat[illegible]nd tested with dilute iodine. A similar set of experiments were mad[illegible]with diastase which had been treated with tricresol for 48 hours.

TABLE XIII

(*A*) Preservative.	Time of action. Hours.	Control.	39 min.	42 min.	43 min.
Tricresol, 0.5%	24	Blue	Brown	Brown	No color
Toluene	24	Blue	Brown	Brown	No color

(*B*) Preservative.	Time of action. Hours.	Control.	36 min.	37 min.	38 min.
Tricresol, 0.5%	48	Blue	Brown	Brown	No color
Toluene	48	Blue	Brown	Brown	No color

EXPERIMENT.[1]

Malt diastase.

0.2 g. of malt diastase was used in each solution, and 25 cc. of 2% starch solution. Otherwise the directions were as given in the preceding experiments.

TABLE XIV

(*A*) Preservative.	Time of action. Hours.	Control.	72 min.	79 min	81 min.
Tricresol, 0.5%	24	Blue	Brown	Brown	No color
Toluene	24	Blue	Brown	Brown	No color

(*B*) Preservative.	Time of action Hours.	Control.	105 min.	111 min.	112 min.
Tricresol, 0.5%	48	Blue	Brown	Brown	No color
Toluene	48	Blue	Brown	Brown	No color

The above results indicate that the action of diastase is not hindered by 0.5% tricresol in 48 hours.

(*g*) *Invertase.*[2]—The activity of invertase was determined by the amount of cane sugar inverted in a given time at 38°, measurements being made with a saccharimeter. The temperature of inversion was kept constant within 0.1° by using a water thermostat. The results are expressed in degrees of rotation.

EXPERIMENT I

(*a*) 30 cc. of invertase solution 4 cc. of 2% tricresol, 6 cc. of water.

(*b*) 30 cc. of invertase solution, 10 cc. of water, 2 cc. of toluene.

Solutions were kept in a incubator at 38–40° and were tested after 24, 48, and 72 hours. 5 cc. of invertase solution (*a*) or (*b*) 100 cc. of 20% sugar solution and 10 cc. of $N/2$ mono-sodium phosphate solution were added together and placed in a water thermostat. At intervals 10 cc. portions were run into 5 cc. portions of strong sodium carbonate solution to stop the inversion and readings were made in a saccharimeter, using a 100 mm. tube.

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[1] Eimer & Amend, Malt diastase.

[2] The yeast invertase was obtained through the courtesy of J. M. Nelson, for which we wish to express our thanks.

TABLE XV.

Preservative.	Time of action. Hours.	Control.	10 min.	20 min.	30 min.	40 min.	50 min.	60 min.
Tricresol, 0.2%	24	20.7	17.0	13.4	9.5	7.2	4.8	[illegible]
Toluene	24	20.0	17.2	13.5	10.3	7.6	5.0	[illegible]
Tricresol, 0.2%	48	20.2	17.0	14.2	11.6	8.6	7.3	4.8
Toluene	48	20.4	17.0	14.2	11.2	8.0	5.6	4.3

The above results indicate that 0.2% tricresol solution does not hinder the action of invertase in 48 hours.

EXPERIMENT II.

0.5% tricresol solution was used in this case, otherwise the directions of the preceding experiments were followed.

TABLE XVI.

Preservative.	Time of action. Hours.	Control.	10 min.	20 min	30 min.	40 min.	50 min.	60 min.
Tricresol, 0.5%	24	20.3	17.7	14.8	12.4	9.5	7.8	5.7
Toluene	24	20.5	16.5	13.0	10.2	6.8	4.3	2.0
Tricresol	48	20.0	18.7	16.5	15.0	14.0	12.3	11.0
Toluene	48	20.4	16.5	13.4	10.6	8.0	6.0	3.3
Tricresol	72	19.0	..	.	.	.	..	18.8[1]
Toluene	72	19.5	17.6	16.8	16.0	14.6	14.0	12.4[1]

The above results indicate that 0.5% solution of tricresol somewhat hinders the action of invertase and that the inhibitory affect is increased with longer standing. No effort was made to maintain a favorable hydrogen ion concentration, which may be the cause of the slight inactivation.

3. Summary.

From the preceding data, it is concluded that tricresol is preferable to toluene, because it is a stronger germicide, and while overcoming the physical and chemical disadvantages of toluene, it does not, in most enzyme work, interfere with ferment action under ordinary conditions. In solutions as strong as 0.5% it can be recommended for trypsin, pepsin, urease and diastase and for erepsin and invertase in 0.2%, during the usual time of incubation. In extreme cases it has a retarding effect as was shown with erepsin and invertase after longer standing with 0.5% solution. With lipase the evidence is contradictory. 0.2% solution of tricresol retards the action of castor bean lipase on ethyl butyrate and triacetin, but seems to accelerate the action of pancreatin on ethyl butyrate and retard the action on triacetin.

For special work, a special preservative may be necessary, but in the usual practical enzyme experiments, tricresol is very satisfactory.[2]

NEW YORK CITY.

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[1] The invertase solutions reached the temperature of 42° in the incubator.

[2] Tricresol ought to be especially useful in preserving specimens for subsequent analysis such as urine, etc., insuring against the loss of preservative by evaporation and permitting accurate volumetric measurement.

THE QUANTITATIVE EXTRACTION OF DIASTASES FROM PLANT TISSUES.

By R. W. Thatcher and Geo P. Koch

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There are two different opinions as to the nature of enzyme action. One supposes that enzymes are only catalytic in their effect, that is, that they are only accelerators of reactions which actually occur in the absence of the enzyme, but at a very much slower rate. The other holds that enzymes are actual causative agents for their specific reactions, and function by forming definite chemical unions with the initial substance which later break down into a new substance or substances, liberating the enzyme unchanged and in condition to repeat the process an indefinite number of times. Whatever may be the nature of their action, however, it is obvious that they do not participate quantitatively in the reaction which is their specific function. Hence, they cannot be measured quantitatively by the usual methods of determining the *quantity of the end-products of the reaction.* It is necessary, instead, to measure their effect upon the *velocity of the reaction.*

In any comparative study of the enzymes of different samples of vegetable materials, it becomes desirable to obtain comparable measures of the quantity of enzyme present. Since there are no known methods for isolating and determining the exact quantity of an enzyme in any given plant or animal tissue and, further, since in the present state of knowledge concerning enzyme action it is uncertain whether the same actual quantity of the same enzyme from different sources will possess the same accelerating or causative effect upon its substrate, the investigator is necessarily forced to assume that the comparative accelerating effect upon reaction-velocity of the extract from the same quantity of the materials under investigation is a comparable measure of the quantity of enzyme present in each sample. Or he may, as is doubtless a better procedure, use as his basis of comparison the "diastatic strength" or some similar term, instead of the actual quantity of enzyme present.

In a series of investigations of the various factors which may influence what is called the "strength" of wheat flour, we have undertaken a study of the enzymes of the wheat kernel and their distribution to the various products separated from it in milling, and of their effect upon the flour during the fermentation of the dough and baking of the loaf of bread. Quite naturally, we first sought to study the diastatic enzymes, that is, those which cause or accelerate the hydrolysis of starch. We were immediately confronted by the lack of a method of quantitative extraction of the active diastases of different samples, which would yield comparable results. There was, first, the question of a suitable standard of measurement of the acceleration of starch-hydrolysis due to the presence of the enzyme, and second, the difficulty of extracting an active hydrolyzing enzyme from a material containing large quantities of the hydrolyzable material, without getting continuous activity of the enzyme during the extraction period. This latter difficulty had led a number [illegible] investigators who had previously attempted a study of this kind to abandon it as incapable of exact solution, since they found that the activity of the enzyme during the extraction "used up" variable proportions of its accelerating effect, and, consequently, they obtained extracts of variable "diastatic strength" from the same sample if the time or temperature of extraction, the ratio of solvent to material, or the conditions of preservation of the extract until its "diastatic strength" could be measured, varied in even comparatively slight degrees. It occurred to us, however, that this difficulty might easily be overcome by carrying out the extraction at a temperature below that at which the enzymes exert any influence upon reaction velocity, say at 0°, provided the enzymes themselves were sufficiently soluble at that temperature to permit the securing of comparably quantitative extractions. This could, of course, be easily ascertained experimentally.

There remained the question of a suitable standard of measurement of the comparative accelerating effect of extracts from different samples. The possibility of comparable measurements depends upon whether the velocity of the reaction is uniform throughout its duration, exhibiting the so-called "straight-line" curve of reaction-velocity, or is modified by the law of mass action, having an approximately logarithmic velocity-curve. In the latter event, it would be impossible to make comparisons of velocity-accelerations of extracts from different samples, as the relative mass of hydrolyzable material and of activating enzyme in each different extract would rarely, if ever, be the same. However, Kjeldahl's first assumption[1] that the amount of reducing sugar produced is a true measure of diastatic power, provided that not more than 40% of the original starch is converted into maltose at the expiration of the period of digestion, has been accepted as a working basis by many investigators and has been indirectly confirmed by Brown and Glendinning,[2] who found that equal amounts of starch were hydrolyzed by diastase in equal times during the earlier part of the reaction, but that toward its close, when the concentration of enzyme becomes large as compared with that of the substrate, the reaction obeys the law of mass action. Kjeldahl's "law of proportionality" was, therefore, accepted as a suitable basis of measurement for our work.

The next question was as to the method of measurement of the velocity of the reaction. Several methods for this have been suggested.

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[1] See *Dingler's polytechn. J*, 235, 379–387, 452–460 (1880).

[2] *J. Chem. Soc.*, 81, 388–392 (1902).

Kjeldahl[1] recommended the determination of the amount of reducing sugar produced by the action of a definite amount of the extract in question upon an excess of starch for a definite length of time at a definite temperature.

Roberts[2] proposed the use of the number of cubic centimeters of a standard starch paste which would be converted into non-iodine-coloring material in five minutes at 40° by one cubic centimeter of the extract under examination, as a standard.

Jungk[3] recommended measuring the time required for 10 cc. of extract, acting at 40°, to convert 10 g. of anhydrous starch into maltose.

Lintner[4] modified the Kjeldahl process so as to make it possible to calculate the diastatic strength upon the basis of the production of a constant quantity of maltose from a constant amount of soluble starch, expressing the "diastatic strength" of the extract in terms of percentage of the strength of a standard diastase, of which 0.12 mg., acting upon a definite quantity of soluble starch for 1 hour at 21°, produced enough maltose to completely reduce 5 cc. of Fehling's solution.

Johnson[5] published a new form of the method, in which the amount of diastase necessary to digest a fixed amount of starch to no color with iodine in ten minutes at a temperature of 40° was determined. He found that the same measure of the velocity of reaction was obtained in this way as by a measurement of the quantity of sugar produced.

Various other modifications of the Lintner process have been suggested from time to time and have recently been submitted to critical review by Sherman, Kendall, and Clark,[6] who recommended, as a result of their studies, the general adoption of 30 minutes as the time and 40° as the temperature for all digestions for the determination of diastatic strength. Their investigations included comparisons of reaction-velocities as measured by the disappearance of iodine-coloring material and by the quantity of maltose produced. Later and more extensive studies of these two methods of estimation of diastatic strength by Sherman and Schlesinger[7] emphasize the distinction between the amyloclastic and the saccharogenic activity of diastatic preparations and point out the relationships which exist between these, and some of the advantages and disadvantages of the two processes.

For the purposes of our investigations, it was very clearly the sugar-producing, or saccharogenic, power of the diastases of flour which it would be of value to study, and we, therefore, decided to use the maltose produced by digestion at 40° for 30 minutes as the measure of the reaction velocity or the "diastatic strength" of the extracts from the samples under investigation.

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[1] *Loc. cit.*

[2] *Proc. Roy. Soc.*, **32**, 145–161; abs. in *J. Chem. Soc.*, **40**, 1051 (1881).

[3] *Pharm. J. Trans.*, [3] **14**, 104–108; abs. in *J. Chem. Soc.*, **46**, 529–531 (1884).

[4] *J. prakt. Chem.*, [2] **34**, 378–394 (1886).

[5] THIS JOURNAL, **30**, 798–805 (1908).

[6] *Ibid.*, **32**, 1073–1086 (1910).

[7] *Ibid.*, **35**, 1784–1790 (1913).

As a rapid and accurate method of measuring the maltose produced, the determination of the residual copper, after boiling a suitable aliquot portion of the solution with a definite volume of standardized Fehling's solution, by titration by the iodine method, as perfected by Peters,[1] seemed promising, and upon trial proved thoroughly satisfactory.

The process of preparing the portion of the extract used as a blank, and the solutions after digestion with soluble starch, for their action upon the standardized Fehling's solution was that used by Swanson and Calvin in their investigation of the conditions affecting the activity of the amylolytic enzymes in wheat flour,[2] and was found to work very satisfactorily.

Experimental Data.

The object of this preliminary work was to ascertain whether the diastases present in wheat-products could be quantitatively extracted at 0°, in order that none of their catalytic power might be "used up" during the process of dissolving them from the material under investigation The plan of the work involved the digestion of weighed quantities of ground wheat, bran, and different grades of flour in water at 0° for varying lengths of time and the determination of the maltose-producing power of the resultant extracts. It was believed that, if the results should show a uniform diastatic power for extracts made at different lengths of time, and a uniform quantity of reducing sugars in the aliquot part of the extract used as a blank, the principle that the diastases are quantitatively extracted, and that nô diastatic action occurs during the extraction at that temperature, would be established.

In order to facilitate computations of fractions resulting from taking aliquot parts, we decided to use 16 g. of material for each extraction. Swanson and Calvin[3] found that the maximum amylolitic activity was secured when flour and water were used in proportions varying from 1 : 4 up to 1 : 10. We, therefore, decided to use 200 cc. of water for each extraction, this being a convenient volume for subdivision and not far outside the optimum limits just mentioned.

Ordinary half-pint milk sample bottles were used to hold the materials during the extraction. These bottles were furnished with a tin cap held down by a spring clamp. To insure against leakage, a disk cut from thin rubber was placed under the cap before it was clamped down. In preparing the material for extraction, the charge of dry material was weighed into the bottle, the cover clamped down and the bottle placed in the ice-water bath until its contents reached the desired temperature. The bottle was then removed from the bath, its stopper loosened, and 200 cc. of redistilled water (previously cooled to 0°) quickly pipetted into it. The cap was again clamped down and the bottle immediately returned to the ice-water bath. The filling of the several bottles of each series was so timed that all the desired periods of extraction would terminate at the same time, in order that all subsequent operations upon the extracts might be carried on simultaneously. Each bottle was shaken vigorously at intervals during the extraction.

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[1] See THIS JOURNAL, 34, 433–452 (1912).

[2] *Ibid.*, 35, 1636–1637 (1913).

[3] *Loc. cit.*

At the expiration of the extraction period, the bottles were removed from the bath and their entire contents quickly poured upon large S and S folded filters. The first few drops which came through were usually cloudy, but by pouring back once or twice a filtrate clear enough for all practical purposes was easily obtained. Filtration was usually rapid enough so that a sufficient volume of extract for the necessary aliquots could be obtained in a few minutes and without serious rise in temperature of the extract. (In working with materials which filter slowly the temperature might be kept down by placing the funnel in a jacket, such as is used for hot filtration, filled with ice-water; but this was not found necessary in any of our work.) As soon as a sufficient volume of extract was secured, it was at once warmed to 40°, the temperature at which its action upon starch was to be ascertained, and two aliquots of 50 cc. each drawn out. To one of these $N/10$ sulfuric acid was added, in such an amount that the resultant mixture would be a 0.02 N solution (this being the strength found by Swanson and Calvin to be the correct one) in order to stop all diastatic action. To the other aliquot, 25 cc. of a 10% solution of soluble starch (previously warmed to 40°) were added, and the mixture placed in an incubator, kept automatically at 40°, for exactly 30 minutes. At the expiration of this time, further action was stopped by bringing the mixture to a 0.02 N sulfuric acid. In both the blank and the digested solution, the soluble proteins were precipitated with salt and phosphotungstic acid, and the maltose in an aliquot of each determined, by the methods mentioned above. The results obtained in the first series of experiments, using ground wheat, ground barley, bran, and three different grades of wheat flour, calculated to the basis of 1 g. of original material in each case, are shown in Table I.

As a further confirmation that the diastases were quantitatively extracted from materials such as those under examination by diffusion into water at 0°, we conducted another series of extractions using in each case, first, the material ground as for ordinary analyses, and, second, the same weight of material after grinding vigorously for ten minutes in a mortar with an equal weight of sharp quartz sand. It would seem that

TABLE I.—SHOWING EFFECT OF DIFFERENT LENGTHS OF TIME OF EXTRACTION AT 0° UPON DIASTATIC STRENGTH OF EXTRACT.

(16 g. material, 200 cc. water, 50 cc. aliquots used.)

Material.	Time of extraction. Hours.	Results calculated to 1 g. material.			
		Copper reduced after digestion. Gram.	Copper reduced by blank. Gram.	Copper due to enzyme. Gram.	Maltose equivalent. Gram.
Wheat	5	0.454	0.023	0.431	0.339
	3	0.422	0.016	0.406	0.319
	1	0.422	0.014	0.408	0.320
Barley	5	0.474	0.038	0.436	0.342
	3	0.465	0.036	0.429	0.337
	1	0.451	0.023	0.428	0.336
Bran	5	0.468	0.008	0.460	0.362
	3	0.434	0.005	0.429	0.337
	1	0.451	0.005	0.446	0.351
Patent flour	5	0.439	0.015	0.424	0.334
	3	0.451	0.013	0.438	0.344
	1	0.477	0.013	0.464	0.365
First clear flour	5	0.445	0.013	0.432	0.339
	3	0.436	0.007	0.429	0.337
	1	0.425	0.005	0.420	0.330
Second clear flour	5	0.477	0.024	0.453	0.356
	3	0.474	0.012	0.462	0.363
	1	0.471	0.007	0.464	0.365

by this vigorous treatment the cell tissues would be so thoroughly ruptured that there could be no possible danger of incomplete solution of the diastases. Two check samples, prepared in this way, of several different materials were treated with water at 0° for $1^1/_2$ hours and the diastatic strength of the resultant extracts determined as before, with the results shown in Table II.

TABLE II.—SHOWING EFFECT OF GRINDING MATERIAL WITH SAND UPON DIASTATIC STRENGTH OF EXTRACT.

Material.	Mode of preparation.	Results calculated to 1 g. material.			
		Copper reduced after digestion. Grams.	Copper reduced by blank. Gram.	Copper due to enzyme. Grams.	Maltose equivalent. Grams.
Barley	ordinary	0.459	0.020	0.439	0.345
	ground with sand	0.474	0.015	0.459	0.361
Wheat	ordinary	0.498	0.023	0.475	0.373
	ground with sand	0.477	0.023	0.454	0.357
Flour	ordinary	0.449	0.015	0.434	0.341
	ground with sand	0.436	0.015	0.421	0.331
Shorts	ordinary	0.965	0.012	0.953	0.736
	ground with sand	0.907	0.020	0.887	0.682
Malt	ordinary	8.433	0.033	8.400	6.460
	ground with sand	8.433	0.035	8.398	6.459

These data clearly indicate a complete extraction of active diastases at 0°. The diastatic strength of the extracts obtained after grinding with sand was sometimes slightly greater and sometimes slightly less than that from the sample prepared in the ordinary manner, indicating that the differences were due to lack of uniformity in the original samples and not to unequal extraction of the active diastases. In other work on similar samples, we were able to make these differences almost completely disappear by long-continued mixing of the material before weighing out samples for the determinations. The extractions for five hours show sometimes a slightly higher, and sometimes a slightly lower, activity than those for one or three hours, indicating that these differences are due to slight variability in the sample or some similar cause, and not to the length of time of extraction.

In each case, a slightly larger amount of reducing sugar was found in the blanks from the longest period of extraction. This might be due either to slight hydrolysis of starch during the extraction, or to slow solution of the reducing sugars in water at this low temperature. It was later ascertained that the sugar in the blank would vary if the proportion of water to material used were varied, while the diastatic activity per gram of material remained practically constant, even though the dilution were doubled or tripled. This clearly indicates that the variation in reducing sugars in the blank is due to gradual solution of the sugars in the material at the low temperature used, and not to diastatic action during the extraction. Further, it was found that the filtered extract could be kept for some hours at the temperature of ice-water without any increase in its sugar content, indicating either that there is no diastatic action at this temperature or that no soluble carbohydrates which can be hydrolyzed by the enzymes present are extracted from these materials at 0°.

In order to be certain that the maltose found was wholly due to diastatic activity, and not to hydrolysis by reagents used in the process or to any other cause, another set of extractions for varying lengths of time was made, using the same samples of ground wheat and barley as in the first series. The only variation in the process was that, just before taking the aliquots of the filtered extract for estimation of its diastatic strength, it was boiled for 10 minutes. The results obtained are shown in Table II.

TABLE III.—SHOWING EFFECT OF BOILING EXTRACTS UPON THEIR DIASTATIC STRENGTH.

Material.	Time of extraction. Hours.	Copper reduced by blank. Gram.	Copper reduced by solution from boiled extract digested with 2.5 g. starch. Gram.
Barley........	2	0 033	0.030
	1	0.030	0.029
Wheat	2	0.010	0 011
	1	0.009	0.010

These results prove conclusively that the hydrolysis of starch to maltose, during the digestion for 30 minutes at 40° in the first series of experiments, was due to the presence of diastases in the extracts under investigation.

Satisfactory results having been obtained with barley and wheat products, it was decided to study the applicability of the process to barley malt. Since malt would certainly contain larger proportions of active diastases than the other materials which had been studied, it was obvious that smaller original weights of material or smaller aliquots of the extract, or both, would have to be used in order to keep a sufficient excess of hydrolyzed starch in the mixture during the digestion period. Several preliminary trials resulted in complete hydrolysis of the starch, even when as much as 5 g. of soluble starch were used with comparatively small aliquots of the extracts. Finally, a new set of extracts was made, using 8 g. malt to 200 cc. water, and a series of mixtures containing 2.5 g. of starch and 1 cc., 2 cc., 5 cc., and 10 cc. of the extract, respectively, were digested at 40° for 30 minutes and the resulting solutions tested with iodine. The solution containing 10 cc. of extract gave no color, that with 5 cc. a puplish red, and those with 2 cc. and 1 cc. a clear blue. It appeared from this that the limit of the reaction would not be reached by using 5 cc of the extract from this particular sample of malt and that 2 cc. of extract would probably bring the conditions within the limits required to insure the operation of "Kjeldahl's law of proportionality."

Accordingly, extractions were made at 0° for varying lengths of time, and in varying volumes of mixture of malt and water, upon two different samples of malt, and digestions of varying aliquots of the resultant extracts with starch carried on as described above. Some typical results of these determinations are presented in Table IV.

In connection with these data, attention should be called to the fact that the very large amount of maltose produced by the action of a very small aliquot of the original extract made it necessary to use a very small fraction of the final solution for the reduction with Fehling's solution. The aliquot of the residual copper solution which was finally titrated with thiosulfate solution corresponded to from 0.01 g. to 0.00625 g. of original malt. Consequently, any slight variation in reading the end point was magnified from 100 to 160 times in calculating the results to the basis of 1 g. of malt.

With this fact in mind, the data in the table clearly show that complete extraction of the enzymes is obtained in a period of one hour or longer. In no case did the three-hour or five-hour extractions give significantly greater "diastatic strength," as shown by the maltose equivalent of 1 g. malt, than was obtained by extracting for only one hour. In some cases, the maltose equivalent was slightly higher in the one-hour extract than in those of longer periods, indicating that the differences were due to experimental error in making the solutions, or to slight variations in composition of the malt. In those cases where the extraction period was shortened to 30 minutes, one of which is included in the table, somewhat lower diastatic strength was always obtained, than in the longer extractions carried on under otherwise identical conditions. It appears, therefore, that this period of extraction is not quite sufficient for complete solution of the diastatic enzymes from materials ground to the customary fineness for analysis.

TABLE IV.—SHOWING RESULTS OF APPLICATION OF PROPOSED METHOD TO ESTIMATION OF DIASTATIC STRENGTH OF BARLEY MALT.

					Results calculated to 1 g malt			
Sample No.	Weight taken. Grams.	Water used. Cc.	Time of extraction. Hours.	Aliquot of extract. used. Cc.	Copper reduced after digestion Grams.	Copper reduced by blank. Grams.	Copper due to enzyme Grams	Maltose equivalent Grams
1	8	200	5	5	8 330	0 090	8 240	6 300
	8	200	3	5	8 120	0 085	8 035	6 140
	8	200	1	5	8 120	0 085	8 035	6 140
	8	200	1/2	5	7 670	0 070	7 600	5 820
1	4	100	5	5	7 840	0 090	7 750	5 940
	4	100	3	5	7 950	0 085	7 865	6 010
	4	100	1	5	8 060	0 085	7 975	6 120
1	4	100	5	2	10 640	0 090	10 550	8 170
	4	100	3	2	10 260	0 085	10 175	7 865
	4	100	1	2	10 080	0 085	9 995	7 730
1	4	100	5	2 + 3*	8 625	0 090	8 535	6 570
	4	100	3	2 + 3*	8 510	0 085	8 425	6 485
	4	100	1	2 + 3*	8 510	0 085	8 425	6 485
2	16	200	5	2	2 620	0 150	2 470	1 935
	16	200	3	5	2 042	0 142	1 900	1 485
	16	200	1	5	2 097	0 117	1 980	1 549

It will be noted that the maltose equivalent per gram of sample was considerably higher when only 2 cc. of the extract were used for the digestion than when 5 cc. were used. This is in harmony with the results of Brown and Glendinning and the assumption of Kjeldahl mentioned in an earlier part of this paper. Evidently, 5 cc. of these extracts hydrolyzed the starch used past the limit of 60% of unchanged starch considered by Kjeldahl as necessary to insure the operation of the "law of proportionality." Further confirmation of this fact is found in the series in which the starch was first digested for 30 minutes with 2 cc. of extract, then 3 cc. more of extract added and the digestion continued for another 30 minutes. The maltose obtained in this way exceeded that obtained by using 5 cc. for 30 minutes, but did not nearly approach the equivalent

* 2 cc. digested 30 minutes, then 3 cc. additional added and digested again for 30 minutes.

amount per gram of malt obtained when only 2 cc. of extract acted for 30 minutes on the same amount of starch.

Since the extracts obtained by treating these various materials with water at 0° obey all the known laws of diastatic action, and since the diastatic strength of the extracts, as measured by maltose produced from a large excess of starch, is the same whether the extraction be continued for one, three, or five hours, we conclude that this method of operation insures a quantitative extraction of the diastases present in vegetable tissues ground to the customary degree of fineness for ordinary analyses. We plan to use this method in our further investigations, and suggest it for trial by other workers engaged in similar studies.

Directions for Use of the Proposed Method.

Prepare the sample whose diastatic strength is to be tested in the same way as for any of the common analytical processes. Weigh a suitable charge, preferably 16 grams or some even fraction thereof, into an 8 oz. wide-mouthed bottle having a water-tight stopper, and immerse the bottle and its contents in ice-water until its temperature reaches approximately 0°. Pipet into the bottle 200 cc. of pure distilled water (redistilled if necessary to insure complete freedom from acid or salts) previously cooled to 0°. Stopper the bottle tightly and immerse it in ice-water for one to two hours, shaking vigorously at fifteen-minute intervals. At the expiration of the extraction, pour the contents of the bottle quickly upon a large folded filter, pouring back the first few cubic centimeters of cloudy filtrate until the extract comes through fairly clear (a perfectly clear filtrate at this point is not absolutely necessary). If filtration should be so slow as to make any considerable rise in temperature of the contents of the filter or of the filtrate probable, place the funnel in a water-jacket filled with ice-water and immerse the receiver in ice-water.

The diastatic strength of the extract should preferably be determined at once. If this is not convenient, however, the extract must be kept at a temperature of approximately 0° until the operator is ready to proceed.

In working with materials rich in diastatic enzymes, it is desirable to make a preliminary test of the approximate amount of starch which will be hydrolyzed by various aliquots of the extract when digested under the standard conditions, in order that the final determination of maltose-producing power may be made with such proportions of volume of extract and starch that not more than 40% of the starch taken will be hydrolyzed during the digestion period. This preliminary test is easily made by measuring the same volume of starch solution that is to be used in the final digestion into each of several test tubes, warming these to 40° then adding varying volumes, say 1 cc., 2 cc., 5 cc., and 10 cc. of the extract, and carrying on the digestion for 30 minutes at 40°. At the end of this time, the solutions are tested with iodine and the one which gives just a faint trace of blue color is regarded as showing the approximate limit of starch-hydrolyzing power of the extract. For the final determination, a volume of extract amounting to approximately 40% of that found as this limit in the preliminary test should be used.

To determine the maltose-producing power of the extract, first warm the starch solution which is to be used[1] to 40°, then pipet the volume of it which corresponds to 2.5 grams of anhydrous starch into a 100 cc. graduated flask. Place this flask in the constant temperature oven kept at 40°. Now warm the extract quickly to 40° and pipet the proper volume of it, as found by preliminary test, or 25 cc. in the case of the common cereals, into the flask containing the starch. Place this flask in the constant temperature oven and immediately pipet another aliquot of the extract into a graduated flask and add standard sulfuric acid to it in such a quantity that when filled to the mark the solution will be 0.02 *N* acid. This solution then constitutes the blank for the determination of reducing sugars already present in the extract. At the expiration of exactly 30 minutes from the addition of the extract to the starch solution, remove the flask from the oven and immediately stop the action by adding sulfuric acid of such strength and amount that the solution when brought to the mark will be 0.02 *N* acid.

To determine the amount of reducing sugars present in the blank and in the digested starch-extract mixture, cool both to room temperature and see that they are made just to the 100 cc. mark; then draw off 50 cc. of each solution and transfer it to another 100 cc. flask; add 25 cc. of a 4% solution of salt and 5 cc. of a 10% solution of phosphotungstic acid, make to the mark and shake vigorously. This precipitates the soluble proteins which would otherwise affect the Fehling's solution. After standing a few minutes the precipitate usually settles, leaving a clear supernatant liquid, an aliquot of which can be drawn off for the estimation of its reducing sugar content; if it does not settle clear, it must be filtered through a quantitative filter before taking aliquots.

The Fehling's reduction may conveniently be carried out in a 200 cc. graduated flask, in order to avoid the necessity of filtering and washing the precipitated cuprous oxide. The small volume occupied by the precipitate does not appreciably affect the volume of liquid in the flask, so that an aliquot may be taken for titration of the residual copper. Measure accurately into the flask 25 cc. of the Fehling's copper solution, add 25 cc. of the alkaline tartrate solution and 50 cc. of water; heat to boiling and then add 25 cc. of the clear filtrate from the protein-precipitation of the solutions under investigation; bring again to boiling and boil for exactly 2 minutes. At the expiration of the 2 minutes, add cold water nearly to the mark and cool the contents of the flask quickly to room temperature and complete the volume to 200 cc. and mix thoroughly. After standing a few minutes the precipitate settles so clearly that 50 cc. of the clear supernatant liquid can usually be pipetted off for titration of the copper which it contains; or the supernatant liquid may be poured through a quantitative filter and 50 cc. of the filtrate pipetted for the titration. The titration should be carried out as recommended by Peters in the article referred to above. At the same time, another 25 cc. of Fehling's solution should be accurately measured into another 200 cc. flask, the volume made up to the mark, and a 50 cc. aliquot pipetted out and titrated for its copper content. The difference between the thiosulfate used for the titration of this 50 cc. and that obtained from the reduction by the solution under investigation gives the thiosulfate equivalent of one-fourth of the copper reduced by the sugar in the aliquot used for the reduction. From these data the maltose content of the digested solution can be computed. From this should be deducted the reducing sugars, calculated as maltose, found in the blank from the same volume of extract as was used for the starch digestion. This gives the maltose produced by the action of the diastases in the volume of extract used. The equivalent amount of maltose reduced by the extract from 1 gram of material can then be calculated, or the data used to calculate the "diastatic strength" of the material to any other basis of comparison which may be selected.

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[1] For the method of preparing soluble starch suitable for this purpose, see the article by Sherman and Kendall previously referred to

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THE ELIMINATION AND RETENTION OF ARSENIC AS DETERMINED BY THE KOCH-NORTON METHOD.

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A great majority of the investigational work on arsenic feeding and poisoning has been done from the physiological and pharmacological standpoint. It had been noticed by Hunter, Brodie and Home[1] that arsenic, when applied to abraided surfaces, passed to the stomach where a specific action was noted. There are many contributions by Rutter, Hugo,[2] Eulenberg, Geis,[3] and others on the physiological action of the drug. Also Esser, Bintz and Arakie[1] have studied the action of arsenic on the tissue. Orfila, Scolosuboff,[4] Ludwig[5] and Chittenden[6] have worked on the elimination and retention of the drug.

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[1] "Poisons, Their Effect and Detection." Blyth, 1906.

[2] *Ibid.*

[3] "Über den Einfluss des Arsens auf den Organismus," *Arch. Path. Pharm.*, 8, 182.

[4] *Bull. soc. chim. belg.*, 24, 124.

[5] *Med. Jahrbuch.*, 1880.

[6] *Am. Chem. J.*, 5, 8.

As Ekeley[1] and others have shown, there is a decided disagreement in the results obtained by the different investigators who have worked on the retention of arsenic in the body. Scolosuboff found the arsenic to be deposited in the largest amount in the spinal marrow; the brain, liver and muscles came next in order. Ludwig, on the other hand, found that the arsenic deposit ran in the following order: liver, kidney, muscle and brain. Chittenden found the greatest amount in the intestines, and the liver, lungs, spleen, stomach and gullet followed in their respective order.

Having used, with much satisfaction, in toxicological work, the Koch-Norton method[2] for the quantitative determination of arsenic in the presence of organic matter, the writers thought that it would be of interest to conduct a short experiment using this method. The method is quite rapid compared to the gravimetric methods and consists essentially in a modification of the Gautier method for the destruction of the organic matter and the subsequent titration of the arsenic with a very dilute iodine solution.

Two dogs were used in the experiment. Dog A was fed 35 milligrams of arsenic trioxide and was killed 24 hours after feeding. The organs were weighed, and analyzed according to the Koch-Norton method. No elimination took place between the time of feeding and killing, consequently all of the arsenic was retained in the body. Upon opening the body, the digestive tract and bladder were found to be absolutely empty, due to the 48 hour fast that the animal underwent previous to the feeding of the drug.

Dog B was also fed 35 milligrams of arsenic trioxide, but was fed and watered in a metabolism cage for 20 days. Urine and feces were collected daily and analyzed. It was found at the end of 20 days that 71% of the arsenic had been eliminated in the urine. In no case, throughout the experiment, was it possible to find arsenic in the feces. On the 21st day Dog B was killed and the same analyses were made as in the case of Dog A.

The urine samples were evaporated to moist dryness and the organic matter destroyed with as small amount of sulfuric acid as possible. In some instances small amounts of nitric acid were added to assist in the oxidation. When nearly all of the sulfuric acid had volatilized, each sample was made up to volume and aliquot parts were taken for analysis. The portions were neutralized with sodium bi-carbonate and titrated with iodine in the usual manner.

The iodine solution was very dilute and was standardized against resublimed arsenic trioxide. One cubic centimeter of the iodine solution was made equivalent to 0.00034 g. of As_2O_3. Blanks were run in every case, on the reagents.

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[1] This Journal, **35**, 483.

[2] *Ibid.*, **27**, 1247.

In the case of the vital organs and feces, a different procedure was necessary. The weighed samples were placed in large casseroles and covered with nitric acid. A few cubic centimeters of sulfuric acid were added and the mixture was allowed to digest on a steam bath. It was necessary to exercise care at this point in order to prevent loss of sample due to rapid oxidation. Stirring was found to be necessary during the first part of the heating.

After the acid mixture had completely liquefied, it was allowed to evaporate to a syrupy consistency, care being taken to prevent carbonization. The liquid was finally heated over a small flame to drive off the nitric acid. Upon dilution with hot water, filtering and washing, the arsenic was dissolved and removed from a large part of the organic matter. The filtrate was evaporated to small volume, digested with sulfuric acid in Kjeldahl flasks and the arsenic determined as in the urine samples.

The following tables show the order in which the arsenic was retained in the various organs:

TABLE I.—SHOWING PER CENT. As_2O_3 IN THE ORGANS.

Dog A 24 hours after feeding.			Dog B. 20 days after feeding.		
1.	Spinal cord	0.0017	1.	Heart	0.0004
2.	Heart	0.0011		Brain	0.0004
3.	Muscle	0.0010	2.	Liver	0.0002
	Brain	0.0010		Intestine	0.0002
4.	Liver	0.0009		Spinal cord	0.0002
5.	Intestine	0.0008		Spleen	0.0002
	Spleen	0.0008		Muscles	0.0002
6.	Stomach	0.0006	3.	Kidney	0.0001
7.	Lung	0.0004		Stomach	None
	Kidney	0.0004		Lung	
8.	Blood	0.0002		Blood	
9.	Skin	0.0001		Skin	

TABLE II.—SHOWING GRAMS As_2O_3 RETAINED IN THE ORGANS.

Dog A. 24 hours after feeding.			Dog B. 20 days after feeding.		
1.	Muscle (305 g.)	0.0030	1.	Muscle (268 g.)	0.0005
2.	Liver	0.0027	2.	Liver	0.0008
3.	Intestine	0.0017	3.	Intestine	0.0006
4.	Blood	0.0016	4.	Heart	0.0004
5.	Skin	0.0014	5.	Brain	0.0003
6.	Heart	0.0009	6.	Kidney	None
7.	Stomach	0.0007	7.	Lung	
8.	Brain	0.0007	8.	Spleen	
9.	Spinal cord	0.0003	9.	Skin	
10.	Spleen	0.0003	10.	Stomach	
11.	Lung	0.0003	11.	Blood	
12.	Kidney	0.0001	12.	Spinal cord	

As was expected, no arsenic was eliminated at any time in the feces. The arsenic that was not eliminated was absorbed rapidly by the tissues.

The elimination ceased to be quantitative so far as the Koch-Norton method was concerned, when about 71% of the arsenic had been eliminated.

Our results indicate that, when arsenic is not fed in sufficient amount to disturb metabolism, it is eliminated in about 15 days.

Although the total weight of muscle was not known, the analyses show that the muscles retained the largest amount of arsenic in grams.

In the case where the dog was killed 24 hours after feeding, the arsenic was found in the largest quantity in the muscle, liver and intestine, in their respective order. The same holds true after an elimination of 21 days has taken place.

When the dog was killed 24 hours after administration of the poison, the blood holds fourth place and the skin fifth place in retention of the drug. After an elimination of 21 days they have had sufficient time to eliminate the arsenic to the point where it could not be determined by this method.

Another interesting fact is brought forth in the table on grams of arsenic retained, namely that the heart, although one of the smaller and least heavy organs, holds sixth place 24 hours after feeding and fourth place at the end of 21 days.

The spleen, spinal cord, lung and kidney are lowest in grams of arsenic retained in both cases. Of course the last mentioned organs hold higher positions in the percentage table but owing to their small weight they do not play an important part in the storing up of the drug in the system.

The tendency of the blood and the skin is to eliminate the poison as rapidly as possible.

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NEW BOOKS.

Vom Kohlenstoff. Vorlesungenen über die Grundlagen der reinen und angewandten Chemie. By HENRI LECHATELIER. Translated by Barschall with a preface by F. Haber. Halle: W. Knapp, 1913. xiv + 324 pp. Price M. 18.

This interesting volume is a translation of the first eighteen lectures of LeChatelier's course in general (*i. e.*, physical) chemistry. They appeared in French in 1908, and the changes from original are very few in number.

In his preface, the author calls attention to the difference between the traditional modes of instruction in physics and in chemistry. In the former science, we deal with facts that can be generalized, and omit the details concerning single substances. We teach the laws and relations, and omit the numerical values of densities, specific heats, and other constants.

Perhaps the tendency to abstractness is carried too far, but the strictly scientific character of the method of instruction is on this account all the more prominent. In chemistry, the opposite course is pursued. Individual experiments, specific reactions, densities and colors of substances, yields, methods of analysis, and technical processes follow one another in endless profusion. The lecture is filled with priceless raw materials for making a science, but the science remains unmade. Chemical dynamics may be discussed, but it is not permitted to overflow its own chapter and affect the dogmatic and scrappy treatment of the other topics.

The author remarks that these methods of instruction in inorganic chemistry have remained unchanged for seventy-five years. This was, and is still doubtless true of France, Germany, and Great Britain. But in the United States the adjustment to a more rational plan had been in progress for many years, and after 1905 began to spread very rapidly.

As we read, we get the impression that we are about to enjoy the perusal of a work on chemistry, constructed on the physics model, yet intended for beginners. But the author, after all, does not attempt this difficult feat. The lectures are evidently intended for advanced students. They constitute a brief treatise on the modern principles of chemistry. They differ from other similar treatises in that the subject is developed in connection with a systematic study of carbon and its inorganic compounds, and is ingeniously interwoven with the descriptive matter. Special attention is given also to the industrial processes into which carbon and its simpler compounds enter. Thus, Moissan's experiments on the artificial preparation of the diamond lead to the discussion of the electric furnace. The various commercial uses of this furnace are described in some detail as they occur. The diamond also introduces color and brilliance, and their physical causes, the relative transparence of diamonds and lead glass for X-rays and the recognition thereby of genuine stones, and the theory of hardness and the methods of measuring it. Hardness, in turn, leads to a statement of the laws of equivalent and additive qualities. The former, like temperatures and hardnesses, can be compared and reproduced, but not measured. The latter, like weights, are additive and can therefore be measured. Similarly the densities of the three varieties of carbon suggest a discussion of the variability of constants like the densities, elasticities, and tenacities of metals when the specimens have been treated in different ways. This illustration is sufficient to show the plan on which the whole subject is worked out. The style is clear, and the treatment suggestive and interesting, as well as novel. ALEXANDER SMITH.

Handbuch der Mineralchemie. DOELTER, *et al* Pts. 3 and 4, Vol. II. Bogen (21–40). Theodor Steinkopff, Dresden and Leipzig. Price, M. 6.50 each.

Herein are treated those minerals of which the meta- and orthosilicates of magnesium, calcium and iron are regarded as the chief constituents.

The strictly chemical knowledge is confined almost entirely to analyses and natural alterations of the minerals. The mass of complex analyses of substances, like the pyroxenes and the amphiboles especially, may well stagger the chemist who is unfamiliar with mineralogy. Questions of formulas and constitution lead only to bewilderment. One feels that the ground must be cleared and drained before this virgin field can be satisfactorily cultivated. The subject is necessarily treated much in the manner of the mineralogist. However, the arrangement is more strictly chemical, the paragenesis is given in greater detail, formulas and constitution are more fully discussed and the most recent data are given. The discussion on p. 635 of Pt. 4 shows how far we are today from a proper understanding of the relations of the numerous constituents in the amphiboles and how important to this understanding synthetic investigations must be. Some inexcusable inconsistencies are found in these pages. For instance, the melting points of tremolites and other amphiboles are given on p. 633, pt. 4, while on p. 635 it is stated that amphiboles are transformed into pyroxenes without melting. On pp. 451 and 457, pt. 3, Doelter doubts the results of other investigators on the transformation of calcium meta-silicate (at 1190°), and remarks that natural wollastonite (the lower form of this silicate) may be heated to 1240° at least, *if it is heated very slowly and for a long time.* These conditions, of course, favor the change at the lowest possible temperature. Here as in previous "hefts" of this book misprints are not uncommon. Slight errors in the spelling of authors' names are of no great consequence, but errors in numerical data which I have noticed in several instances are much more serious. It is to be hoped that mistakes in data and references are unusual, since the chief value of the books rests on these.

The same. Pt. 2, Vol. III. Bogen (11 20). Price, M. 6.50. The contents of this "heft" possesses great variety and more chemical data than the above. Minerals containing the rare elements of the third, fourth and fifth groups of the periodic system are considered, together with a good deal on analytical procedure. Native tin, lead, their oxides and the thorium minerals are included. In connection with the last is a section on radioactivity and its significance for mineral chemistry by St. Meyer, of Vienna. The natural nitrates, especially Chili saltpeter, their occurrence, composition and theories concerning their formation are discussed, and a considerable body of physico-chemical data is given. The phosphates also are begun in this "heft." E. T. ALLEN.

Quantitative Chemical Analysis. Adapted for Use in the Laboratories of Colleges and Technical Institutes. By FRANK CLOWES, D. Sc Lond., and J. BERNARD COLEMAN, A. R. C. Sc. Dublin. 10th ed. 577 pp. P. Blakiston's Son & Co., Philadelphia. 1914. Price, $3.50 net.

The present edition of this text has been carefully revised and certain new matter introduced "which includes a new form of oven for drying at constant temperature; the analysis of commercial aluminum and bauxite; additional methods for the estimation of titanium in iron ores, of phosphorus and manganese in iron and steel, and of moisture in coal; and a recent method by Blichfeldt for the detection and estimation of foreign fats in butter."

The text is comprehensive in its scope. After a discussion of the technique of chemical analysis and a presentation of the standard methods of gravimetric and volumetric analysis, a large number of technical procedures are given in detail. These include the analysis of such materials as the most important minerals and ores, alloys, water, fuels, foods, oils and fats, soap and gases.

The directions are clear and concise, without having been too much curtailed, and are preceded by a discussion of the principles involved in the method. The printing and the illustrations are good, and the text free from typographical errors.

The omission of several methods of analysis that have become standard, is unfortunate. Among these are the modified Kjeldahl method for use in the presence of nitrates, the colorimetric determination of titanium, volumetric methods for the determination of phosphorus in iron and steel, and the use of the Orsat apparatus.

Many teachers will object to writing "Am" for the ammonium radical in the formulas of ammonium hydroxide and ammonium salts.

For use in American laboratories the bibliography could be profitably extended, particularly with reference to some of the bulletins of the United States Government.

These are minor details, however; the text is an excellent one for the teacher, the student, or the analyst. That it has found a place among the standard works on quantitative analysis is evidenced by the appearance of three editions during the last four years. JAMES H. WALTON, JR.

Chemistry, Inorganic and Organic. By CHARLES LOUDON BLOXAM Tenth edition, rewritten and revised by A. G. BLOXAM AND S. J. LEWIS. Philadelphia: P. Blakiston's Son & Co. pp. xii + 878, 24.5 × 15 cm. Price, $5.50 net.

All chemists will welcome the appearance of the tenth, revised, enlarged, and largely rewritten edition of this well known book. The number of pages remains the same, but the type-page has been enlarged so that the amount of reading matter is twenty-eight per cent. greater. The book as it now stands contains introductory matter (13 pp.) which is very condensed, non-metallic elements (280 pp.), general principles and physical chemistry (60 pp.), metallic elements (180 pp.), organic chemistry (285 pp.) and index (56 pp.). No other work on the science embraces, in one volume, information which is so varied, so well proportioned and so complete. The names of the revisers guarantee due attention to processes and principles of technical interest, while modern views have not been neglected. The book will be found to offer a valuable work of reference alike for teachers, students, and industrial chemists.

In the descriptive portions, many of the less common compounds are discussed, as well as the well known ones. In the theoretical portion the modern principles are set forth briefly but clearly. The organic section constitutes, in itself, an admirable elementary treatise on the subject. In the latter, aromatic and fatty compounds are treated together, general matters such as boiling points, freezing points and specific volumes of the various series of compounds receive attention, and special topics such as the constitution of benzene and stereoisomerism are discussed fully.

There are some features which one would have wished to see improved. Valency is first stated to be a form of chemical energy, although later the correct view is presented. Chlorine-water bleaches even in the dark "because the coloring matter, being ready to combine with the oxygen, exerts attraction on the oxygen of the water, etc.," and not because it contains hypochlorous acid whether it is illuminated or not. That chlorine, hydrogen chloride, and other substances form hydrates is mentioned in each case under the physical properties. That the vapor of the calomel has been shown to consist wholly of mercury and mercuric chloride seems to have escaped notice. Slight blemishes like this, however, are more than offset by the much more numerous instances in which the sound views and recent results are given. The chief fault is the common one, namely that the principles are confined to their special section and do not affect the systematic treatment. Thus, complex ions are discussed (p. 331) and reference is made to cobalt compounds (p. 458). But on the latter page, the formulas given indicate nothing more definite than ammonia of crystallization. Similarly, under potassium ferrocyanide, which is treated in the organic section, the only reactions discussed are those which might characterize a double salt, and under cuprous chloride we learn that it dissolves in solutions of alkali chlorides giving soluble double chlorides such as $CuCl, 2KCl$. The uninstructed reader is little likely to get correct views from such antiquated and largely misleading ways of presenting the facts.

ALEXANDER SMITH.

A New Era in Chemistry. By HARRY C. JONES. New York. D. Van Nostrand Company, 1913. pp xii + 326. 14 × 20 cm. Price, $2.00 net

The new era referred to in this title begins with 1887, the year of the appearance of the first volume of the *Zeitschrift für physikalische Chemie*, and the scope of the work can best be indicated by quoting the titles of its twelve chapters: Condition of chemistry in 1887; development of the law of mass action; the energy changes that take place in chemical reactions; van't Hoff, LeBel and Guye and the origin of stereochemistry;

the phase rule of Willard Gibbs; chemical dynamics of van't Hoff and chemical equilibrium of Le Chatelier; the role of osmotic pressure in the analogy between solutions and gases; Arrhenius and the theory of electrolytic dissociation; the solvate theory of solution and the importance of solutions for science in general; the work of Wilhelm Ostwald in inaugurating the new era in chemistry; investigations by the students and co-workers of Wilhelm Ostwald; the electron and radiochemistry.

This is a very readable book, the style being somewhat conversational, like that of a lecturer talking in a friendly way to a small class. Some of the evils of this style are occasionally noticeable in the way of repetitions, more necessary in lecture notes than in a printed book; but this makes the reading the more easy. One is occasionally roused to refocus one's consciousness, however, as when the eye encounters a paragraph on p. 253, whose first sentence reads: "Osmotic pressure is the cause of diffusion;" and whose last sentence runs: "Set these [lead cylinders] aside for a few years, when it was found that the gold had penetrated the lead to a depth of several millimeters." But in general the reading is perfectly comfortable, and those who would cavil at questions of emphasis or sins of omission should remember that everyone is entitled to his own viewpoint. One of many possible suggestions would be that it might be helpful to introduce the idea of concentration in dealing with the law of mass action.

The contents are necessarily a little too technical to appeal to the general reader or even to the beginner in chemistry without some previous knowledge of the subjects dealt with; but the book should be useful to those more advanced and discriminating students of chemistry who would willingly be reminded, informally and with not too much effort on their own part, of a number of things that they studied in their more formal text-books; and to such students the book may be recommended.

ALAN W. C. MENZIES.

The Use and Care of a Balance. PETER J. KAYSER. The Chemical Publishing Co Easton, 1913. 42 pp. Price, 75 cents.

The author of this little book has had fourteen years of experience in making and adjusting analytical weights under an eminent maker, and ten years' experience in visiting laboratories as an adjuster of balances and weights. He carefully describes the process of setting up a new balance for use, and of testing zero point, equality of arms, and sensitiveness. Instructions are then given for the improvement of a balance whose adjustment has become imperfect through use, as far as this can be undertaken by the owner without recourse to the maker. A few pages are devoted to the care and verification of weights.

The book is likely to be useful in laboratories, both commercial and educational, and may be commended to such. EDWARD W. MORLEY.

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HYDROLYSIS OF RARE EARTH SULFATES.

BY S H KATZ AND C. JAMES

Received March 5, 1914.

Stock[1] determined aluminum by precipitating the hydroxide with potassium iodide and potassium iodate according to the equation, $Al(SO_4)_3 + 5KI + KIO_3 + 3H_2O = Al(OH)_3 + 3K_2SO_4 + 3I_2$. The hydroxide was then ignited and weighed. He found it was advantageous to have sodium thiosulfate, or excess potassium iodide, present during reaction to prevent precipitation of solid iodine, which, he said, interfered with subsequent working with the aluminum hydroxide.

Moody[2] found that the quantity of iodine, liberated by Stock's reaction with aluminum sulfate, was only about two-thirds of the theoretical amount. When this iodine was removed with sodium thiosulfate, more was liberated. When the solution of potassium iodide, potassium iodate and aluminum sulfate was heated in a current of hydrogen, or steam, for fifteen to twenty minutes and the volatilized iodine collected in potassium iodide solution, titration of the iodine in the receiver and that left in the distilling flask furnished a means of estimating aluminum. Later Moody[3] found that stannic salts and those of nickel, cobalt and chromium reacted quantitatively, and, as in the case of aluminum, the liberated iodine, when collected and titrated, afforded a means of estimating the quantity of metal. Though zinc gave only 80.1% of the theoretical amount of iodine, this percentage was constant. Thus Moody was enabled to estimate zinc too by this method.

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[1] *Compt. rend.*, **130**, 175 (1914).

[2] *Am. J. Sci.*, **20**, 181 (1905).

[3] *Ibid.*, **22**, 176 (1906).

That the bases of the different rare earths differ greatly in strength, is well recognized. Meyer[1] states that there are probably two series of earths when arranged in order of their decreasing positive character:

+ La, Ce, Pr, Nd, Sa,—
+ Y, ---Gd, Tb, Er, Yb, ---Sc—.

Boisbaudran[2] states that, on purifying gadolinium by fractional precipitation of the hydroxides with dilute ammonium hydroxide, he found samarium concentrated in the head fractions and didymium in the tail. Assuming that the un-ionized hydroxides have the same order of solubility, which is very small in comparison with the solubility of the ionized hydroxides, Boisbaudran's results would indicate that gadolinium hydroxide is a stronger base than samarium hydroxide. Its ions maintain equilibrium with a greater concentration of hydroxyl ions than the samarium ions. Benedicks[3] also found that, in the purification of gadolinium by fractional precipitation with dilute ammonium hydroxide, samarium was concentrated in the first fractions.

Experimental.

Apparatus.—The apparatus used in carrying out the experiments herein described is a modified form of that used by Moody[4]. The steam generator consisted of a globular flask provided with a thistle tube and an exit tube for the steam. The exit tube was connected to a three-way tube, of which one arm was closed by a cork stopper. Distillation could be interrupted by removing the cork and allowing the steam to escape into the air. The third arm was connected to a tube which led to the bottom of a 500 cc., side-tubed distilling flask. The exit tube of the distilling flask was joined to a glass condenser, and another condenser of the same kind was attached to the first condenser. At the end of the second condenser was an adapter for leading the distillates into two hundred and fifty cubic centimeter, graduated flasks in which they were collected and measured. The necks of the graduated flasks were so flanged that, between the flask and the adapter, solid, moistened potassium iodide could be placed for extracting the iodine from the atmosphere displaced from the flasks. All joints in the apparatus were made of cork.

Solutions.—According to Stock's equation, $M_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2M(OH)_3 + 3K_2SO_4 + 3I_2$, one molecule of $M_2(SO_4)_3$ will react with five molecules of KI and one molecule of KIO_3. One gram atom of iodine is then equivalent to one-sixth of a gram molecule of $M_2(SO_4)_3$, five-sixths of a gram molecule of KI and one-sixth of a gram molecule of KIO_3.

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[1] Die Analyse der Seltenen Erden und die Erdsäuren, p. 32.

[2] *Compt. rend.*, 111, 393 (1890).

[3] *Z anorg. Chem.*, 22, 398 (1900).

[4] *Loc cit*

Solutions were in most cases prepared in small quantities at a time. In making them the proportions expressed by the following figures were used:

Eight-tenths normal solution of potassium iodide was made by accurately weighing $^8/_{10} \times {}^5/_6 = {}^2/_3$ of the gram molecular weight of chemically pure potassium iodide, dissolving and diluting to one liter.

Eight-tenths normal solution of potassium iodate was made by accurately weighing one-sixth of the gram molecular weight of chemically pure potassium iodate, dissolving and diluting to one liter.

Eight-hundredths normal solutions of the various rare earth sulfates were prepared and standardized as follows: Solutions of the purest rare earths available were treated with oxalic acid in excess and the resulting oxalates ignited to oxides. The oxides were dissolved in a slight excess of dilute hydrochloric acid and the solution filtered. Sulfuric acid, in small excess of that required to combine with the oxides used, was then added and this solution poured into a large excess of alcohol. As the hydrated sulfates dissolve very slowly, those obtained were dehydrated by heating in an oven to temperatures not in excess of 250°. The dehydrated salts were dissolved in water and diluted so that the concentration did not become lower than 0.08 normal. Two portions of 25 cc. were measured with pipet, the earth precipitated as oxalate and weighed as oxide. From the results the volume of solution required to furnish salt for 250 cc. of 0.08 normal solution was calculated. This was accurately measured and diluted to 250 cc.

A 0.1 normal solution of sodium thiosulfate was prepared and standardized by the usual methods.

In making all solutions the water used was boiled to expel carbon dioxide and other dissolved gases.

Procedure and Results. 50 cc. of the 0.08 N rare earth sulfate solution, 50 cc. of boiled water, 10 cc. of 0.8 N potassium iodide and 10 cc. of 0.8 N potassium iodate solution were mixed in the distilling flask of the apparatus. If the rare earths contained were completely hydrolyzed to hydroxide, with liberation of the equivalent quantity of iodine, 40 cc. of $1/N$ sodium thiosulfate solution would be required to titrate the iodine produced. The 10 cc. of the iodine solution and the 10 cc. of the iodate solution furnished twice the theoretical quantities of these reagents required for the complete reaction with the rare earth sulfates.

In carrying out the experiments, it was found that equilibrium of the reaction had practically been reached by the time 1250 cc. of distillate had collected. Also, that increasing the volume of solution, in which hydrolysis was taking place, decreased the quantity of iodine liberated in a given volume of distillate. On the other hand, decreasing the volume increased the quantity of iodine, and the slower the distillation proceeded, the more iodine was delivered per unit of distillate.

To overcome these variations, the distilling flask was marked at the height at which it contained 120 cc. A burner with a small flame, which could be regulated, was placed under the flask to compensate for condensation. Although the solution was agitated by passing steam, it was possible after some trials to maintain the volume constant within limits of 10–20 cc. Small increases and decreases in volume, which alternately occurred, served to compensate each other during the distillation of the entire 1250 cc. The rate of distillation was regulated so that each portion of 250 cc. was obtained in as nearly thirty minutes as possible. The time required for obtaining the entire distillate was recorded.

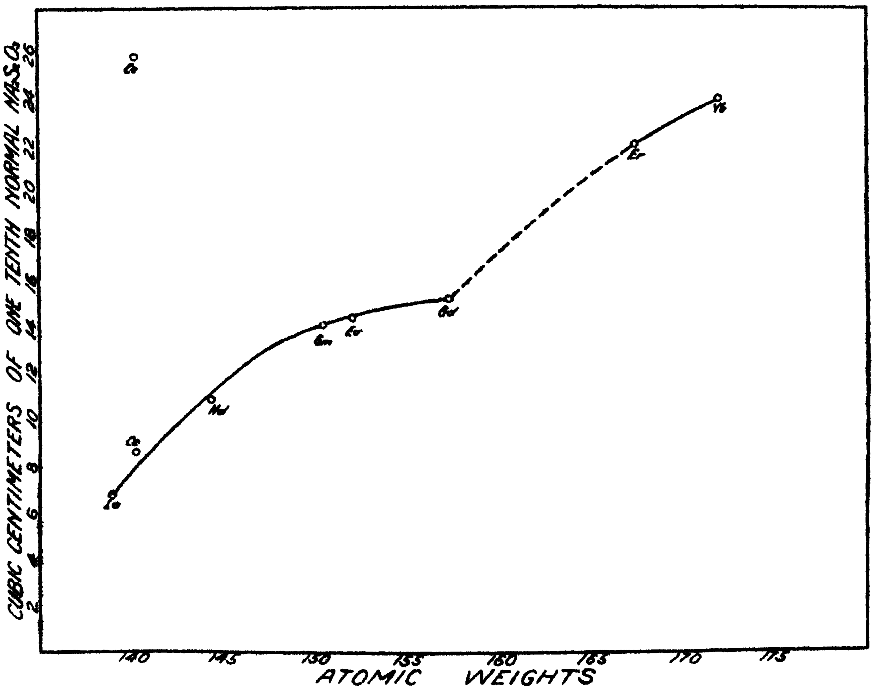
During the first part of the distillation of the solutions of earths of higher molecular weight, much solid iodine was collected in the condenser. While the first portion was being distilled, cooling water was run through the second condenser only. When 250 cc. of distillate were obtained, water was run through the first condenser, the two condensers were disconnected, an adapter was attached to the first, and the process carried on as before with the use of one condenser only.

Cerium acted in the same manner as the other earths during the distillation of the first 750 cc. But while the fourth and fifth portions were being obtained, cerous compounds were oxidized to ceric. The ceric compounds readily hydrolyzed with liberation of much iodine. A sixth portion of 250 cc. of distillate, collected from the experiment with cerium, showed that reaction had almost ceased after the distillation of 1250 cc. Using the values obtained from the first, second and third portions of distillate from cerium, and for the fourth and fifth, averaging the values obtained from the corresponding portions from lanthanum and neodymium, a summation in accordance with those of the other elements was obtained.

In securing the first results by the process of distillation, conditions were not standardized. However, the same general relations in results were obtained from the different elements, as are given in the figures following, these figures being secured under regulated conditions. This table shows the atomic weight of each rare earth used, the time required for the complete distillation process, the volume of solution in the distilling flask at the conclusion of the experiment with each earth, the volume of 0.1N sodium thiosulfate solution required to titrate each 250 cc. portion of distillate and the total thiosulfate required for the experiment with each earth, DATA FROM EXPERIMENTS.

$M_2(SO_4)_3$	Time Hr.	Time Min.	Final volume in distilling flask in cc	Cc. of 0.1 N thiosulfate used to titrate each portion of distillate. No. 1.	No. 2.	No. 3.	No. 4	No. 5	No. 6.	Total thiosulfate solution.
$La_2(SO_4)_3$......	2	34	130	2.98	1.85	1.22	0 44	0.32	.	6.81
$Ce_2(SO_4)_3$......	2	42	100	4.80	1.89	1.23	6.53	11.23	0.17	25.90
$Nd_2(SO_4)_3$.....	2	34	130	7.99	1.68	0.55	0.37	0.48	..	11.07
$Sa_2(SO_4)_3$......	2	36	120	8.58	4.24	0.51	0.38	0.27	..	14.04
$Sa_2(SO_4)_3$......	2	34	115	10.97	1.86	0.71	0.47	0.35	..	14.36
$Sa_2(SO_4)_3$......	2	34	135	11.57	1.25	0.60	0.56	0.37	..	14.35
$Eu_2(SO_4)_3$......	2	33	130	10.84	1.40	0.89	0.71	0.66	..	14.50
$Eu_2(SO_4)_3$......	2	32	130	11.49	1.77	0.74	0.66	0.46	..	15.12
$Eu_2(SO_4)_3$......	2	33	130	9 52	1.80	1.00	0.90	0.83	..	14.05
$Gd_2(SO_4)_3$.....	2	33	135	11 84	1.71	0.71	0.42	0.42	..	15.
$Gd_2(SO_4)_3$....	2	35	130	11.55	2.28	0.61	0.53	0.58	..	15.5510
$Er_2(SO_4)_3$.....	2	33	110	17 92	2.17	0.81	0.64	0.51	..	22.05
$Yb_2(SO_4)_3$.....	2	33	130	21 20	1.57	0 58	0.40	0.26	..	24.01

In the accompanying diagram the atomic weights of the rare earths are the abscissae and the total number of cc. of 0.1 N sodium thiosulfate solution used in titrating the distillates from each earth are the ordinates. When more than one experiment was made with an element, the average of the results is plotted on the diagram.



As no elements with atomic weights between those of gadolinium and erbium were available for this work, a dotted line is used in this portion of the curve.

Conclusions.

It will be noticed that, although sulfates of samarium, europium and gadolinium gave approximately the same results, the tendency to hydrolyze throughout the series increased with increase in atomic weight.

Meyer[1] includes yttrium in his series. This element has an atomic weight of 89 and can not fit the curve formed by the rare earths, so it has not been used in this work. Considering actual rare earths, no sharp division of the elements into two series, when comparing basicity with atomic weights, has been found.

The results of this investigation indicate that, in the purification of gadolinium from samarium by fractional precipitation with ammonium hydroxide, the samarium would be concentrated in the tail fractions and not, as found by Boisbaudran[2] and Benedicks,[2] in the head. Concerning this difference the authors have at present nothing further to offer.

DURHAM, N. H.

ELECTROSTENOLYSIS.[3]

BY HARRY N. HOLMES

Received March, 4, 1914

Historical.

Braun and Coehn, who have done most of the work in this subject, made their capillaries by heating thick glass tubes, closed at one end, and plunging them into cold water. The tubes were shivered into a number of fine cracks which were really capillary spaces. A platinum anode with a water solution of some salt was placed in this tube, which rested in a beaker containing more of the same solution and the platinum cathode. On passing through a direct current at 40 v. or more, preferably 110 v., a spongy deposit of metal or oxide was found in the cracks.

Coehn[4] explained this phenomenon on the assumption that, when two substances are brought into contact with each other, the one possessing the higher dielectric constant will become positively charged. Since water has a very high dielectric constant it must be positive to most insoluble substances. The layer of water in contact with the walls of a glass capillary is positive and, under the influence of an electric current of sufficient voltage, must be attracted to the cathode leaving the glass wall of the capillary negatively charged. This negative charge increases to a point where it is great enough to discharge positive ions present, causing a deposit of metal or oxide in the capillary. Coehn believed that the deposit must always be slight because of the relatively heavy charge on the ions and small charge on the capillary wall. In most cases any minute deposit that may form can not increase to an appreciable amount because it takes part in conduction of the current, one end becoming an anode and losing as fast as the cathode end gains. Yet there are cases where this initial deposit increases to visible size. According to Coehn such cases are:

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[1] *Loc. cit.*

[2] *Ibid.*

[3] By electrostenolysis is meant the deposition of a metal or its oxide in very fine capillaries when the solution filling these capillaries is electrolyzed. Frequently there is an evolution of gas from the deposit

[4] *Z. Elektrochem.*, 4, 501 (1898); *Z. physik. Chem.*, 25, 651 (1898).

1. When the deposited metal is not oxidized at the anode as, for example, the platinum salts.

2. When an insoluble compound is formed at the anode, especially the peroxides.

3. When, in the case of salts in the lower state of oxidation, the negative ion can react with the solution with the formation of a higher oxidized salt; as in the case of a cuprous chloride solution. Here the chlorine liberated oxidizes the salt to cupric chloride.

4. Coehn[1] developed a qualitative test for cobalt in the presence of nickel salts and also a tedious quantitative separation of the two metals based on his observation that cobalt salts showed stenolysis, while nickel salts did not.

Richards and Lacy[2] proved that the complication of electrostenolysis does not affect the weight of the true cathode deposit or the exact application of Faraday's law.

Braun[3] obtained the following results:

Stenolysis with water solutions of

$Co(NO_3)_2$
$Pb(NO_3)_2$
$Pb(Ac)_2$
H_2PtCl_6
$HAuCl_4$
$Pd(NO_3)_2$
$Th(SO_4)_2$

$AgNO_3$
Ag_2SO_4
$AgAc$
$FeSO_4$
Na_2PtCl_6
Cu_2Cl_2

No stenolysis with salts of

Ni
Zn
Bi

Cu (except Cu_2Cl_2)
$KAg(CN)_2$
$FeCl_3$

The effective capillary surfaces in tubes prepared by Braun's method are very limited, offering great resistance to the passage of the current and yielding smaller deposits than are desirable. Furthermore, it is not easy to examine the deposits chemically and the preparation of the tubes is tedious. In all cases the walls of the capillaries are glass. To devise more effective and convenient methods for studying this highly interesting phenomenon this work was undertaken.

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[1] *Z. anorg. Chem.*, 33, 9 (1903).

[2] THIS JOURNAL, 27, 232 (1905).

[3] *Wied. Ann.*, 42, 450 (1891); 44, 473 (1891).

Experimental.

Braun's method of preparing cracked glass tubes was duplicated, though at first only a small percentage of the tubes prepared were of any service whatever. On plunging the hot glass into cold water the tubes frequently broke into pieces, or the cracks were so wide as to leak rapidly or were mere surface fractures.

Repeated trials proved that soft glass tubing 2 3 mm. thick was most suitable. The closed end should not have too thick a mass of glass and, in general, it is safer to heat at a little distance from the closed end. The temperature requisite can only be determined by experiment. The glass must be just hot enough to shiver it into a network of fine cracks on quenching in water, but not hot enough to cause the tube to fall into pieces. A little practice enables one to prepare tubes with a beautiful lace-like surface and with capillaries so narrow that the tube will not leak more than a drop in an hour.

Using these capillary walls to separate anode and cathode, nearly all of Braun's experiments were readily duplicated. Solutions of cobalt chloride and cobalt nitrate quickly yielded black deposits with a direct current of 110 v. The cobalt deposit was fairly compact and formed in the crack, but the lead deposit was very spongy and appeared on the edge of the cracks nearest the anode. Solutions of chloroplatinic acid yielded most spectacular results, as the deposit spread from one crack to another forming a platinum mirror over the surface of the glass. Deposits of other metals were less striking, frequently extremely minute. Gassing from the cracks was common.

It was evident that an increase in the number of capillaries would give promise of increased deposits and with this in view glass tubes, U-shaped, were packed with various finely powdered insoluble substances and filled with water solutions of various salts to be tested by electrolysis. Naturally, glass powder was tried first and then precipitated and ignited silica. These were followed by flowers of sulfur, arsenic trisulfide, calcium fluoride, aluminium trioxide, lead sulfate, asbestos, shellac, kaolin, chromic chloride (violet) and starch paste. Of this list, powdered glass, sulfur and silica proved to be the best. In fact, no deposit at all could be secured in calcium fluoride, aluminium trioxide, lead sulfate, kaolin, starch paste and arsenic trisulfide. Possibly longer running may produce deposits with some of these powders.

With glass powders, the nature of the charge developed in contact with solutions is the same as with capillary cracks in glass tubes, but the surface exposed is enormously greater. Glass powder in water is sufficiently alkaline to precipitate many metallic hydroxides.

Sulfur possesses the advantage of a color that contrasts well with most stenolytic deposits and it can be secured in a finely divided form. Solutions diffuse through it so slowly that soaking for some hours is advisable before attempting electrolysis.

Silica, in the precipitated and ignited form, affords very fine capillary spaces and is free from the alkalinity of glass powder. Its white color is a distinct advantage.

To prepare the porous membranes, a soft glass tube about 1 cm. inner diameter was bent into a U about 8 cm. high. This was then packed with the proper dry powder for a length of about 5 cm. and the membrane held in place by two compact plugs of washed asbestos about 1 cm. deep. Without these asbestos plugs some light powders spread through the solutions. Finally the tube was filled with the solutions to be examined and platinum electrodes suspended in the liquid above the asbestos. A direct current at 110 v. was passed for a few minutes or several hours as required. The current strength varied from a small fraction of an ampere to two or three amperes. No attempt was made to study quantitatively the effect of variations in the current strength.

Objection may be raised that deposits near the electrodes could be accounted for by the droppings from these electrodes. This objection was met by using very compact powders and reporting only such deposits as appeared midway between the electrodes. Duplicates were also run with the U tubes inverted over beakers of the solution used. Deposits on the main electrodes could not possibly get into the membrane.

An important variation in the method of preparing the membranes consisted in packing the U tube with layers of different insoluble powders. A combination frequently used was asbestos plug, powdered glass, sulfur, silica and asbestos plug, in the order named. The yellow color of the sulfur aided the eye in marking boundaries. The deposit could generally be seen at the surface of the glass tube but in some cases the tube was broken at previously made file marks and the entire powder examined.

In addition to the results obtained by Braun, stenolytic deposits were secured with dilute water solutions of

Cu_2Br_2 in SiO_2 and glass powder
Cu_2I_2 in SiO_2 and glass powder
$CuSO_4$ in glass powder
Fehling's solution in glass powder
Na_2SnO_2 in glass powder
Na_2PbO_2 in glass powder
$(NH_4)_2MoO_4$ in S and SiO_2
$NiBr_2$ in glass powder
$MnCl_2$ in S

With a cracked glass tube prepared in the old way a distinct deposit of nickel peroxide was secured with a solution of nickel sulfate. Braun reports that he failed to obtain such a deposit. Another interesting result was the stenolytic discharge of bromide ion in glass powder and in sulfur. This was observed when electrolyzing cobaltous bromide solution several hours in sulfur and nickelous bromide in glass powder. In each case the bromine appeared around a small deposit of the metallic peroxide. The explanation is, of course, that the cobalt or nickel deposit became an intermediate electrode, with one end acting as cathode to the main anode and the other end as anode to the main cathode. The bromide ions were discharged at the anode end of the peroxide deposit. To test this explanation a short piece of platinum wire was imbedded in the sulfur membrane at some distance from the electrodes. Electrolysis of any bromide solution produced a quick appearance of bromine at the anode end of the platinum wire.

After a few hours, a distinct deposit of cobalt peroxide was secured with alternating current using cobaltous bromide in sulfur.

Coehn's theory of electrostenolysis leads one to expect that a compact membrane of any insoluble powder which is negative to water must be able to discharge positive ions during electrolysis. The list of observed deposits is short. A complicating feature is the property which some insoluble substances have of assuming a positive charge in some solutions and a negative in others. Sulfur, silica, glass, kaolin, most sulfides, and asbestos are negative to water; so the first deposit in such membranes must consist of metal or oxide. However, after such a deposit has begun it may cause the discharge of negative ions by its anode action. There are comparatively few insoluble substances positive to water. These include some metallic oxides and sulfides, lead sulfate, barium carbonate and chromium chloride (violet). Aluminium trioxide, lead sulfate and chromic chloride were tried without success. No negative metallic deposit was expected in them but it was thought possible that the bromide ion might be discharged and seen in such a white positive membrane as aluminium trioxide. None was obtained.

Summary.

The main purpose of this research was to develop a method for studying electrostenolysis on a larger scale than before. Some additional results of interest were obtained but no attempt was made to study variations in concentration, the solvent, voltage or current strength.

1. Deposits of metallic oxides and metals, due to electrostenolysis, were greatly increased by the use of capillary membranes in the form of glass tubes packed with such finely powdered substances as glass, sulfur and silica. The ease with which these tubes could be broken in sections

and the contents examined was a distinct advantage. By Braun's method, glass capillaries were the only ones possible but this improvement permits the use of any number of insoluble substances for a membrane.

2. In addition to the results obtained by Braun, electrostenolytic deposits were secured, by the new method, in water solutions of cuprous bromide, cuprous iodide, copper sulfate, Fehling's solution, sodium plumbite, sodium stannite, ammonium molybdate, manganese chloride and nickelous bromide. These results were secured with direct current at 110 v., but a deposit was also secured in a cobaltous bromide solution using alternating current.

A discharge of bromide ion was observed around an initial deposit of cobalt peroxide formed by electrostenolysis.

EARLHAM COLLEGE, RICHMOND, INDIANA.

THE ELECTRON CONCEPTION OF VALENCE.

BY STUART J BATES

Received February 27, 1914

There is one point of considerable importance in connection with this theory to which it appears desirable to call attention in view of the recent discussions of this topic in THIS JOURNAL. Comparatively recent works in physics has caused physicists to reconsider the validity of the assumption that "every chemical bond formed between two atoms involves the transfer of a corpuscle from one atom to the other."[1] Thus Sir J. J. Thomson, who proposed and first developed the electron theory of valence, has, chiefly as a result of his investigation of positive rays, changed his opinion regarding the mechanism of the attraction between atoms. "We are led by these results to regard the electrical forces which keep the atoms in a molecule together as due not to one atom being charged positively and the other negatively, but to the displacement of the positive and negative electricity in each atom. Thus each atom acts like an electrical doublet, and attracts another atom in much the same way that two magnets attract each other."[2]

The objections which may be raised against the electron theory of valence are probably much less widely known among chemists than is the evidence in favor of it. It seems worth while to indicate the nature of a few of these objections without attempting to develop them here:

(1) It is difficult to conceive of the two atoms in the molecule of an elementary gas as hydrogen, or of the two methyl groups in ethane, as being so different from one another as would be the case if one half of the mole-

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[1] Nelson, Beans and Falk, THIS JOURNAL, 35, 1810 (1913).

[2] J. J. Thomson, "Rays of Positive Electricity" p. 66, (1913), Longmans, Green & Co. See also *Phil. Mag*, 24, 249 (1912).

cule is positive and the other negative. In the vast majority of reactions the two halves of such molecules react in an identical manner.[1]

(2) The electron theory of valence predicts a much greater number of isomeric compounds, even among relatively simple organic substances, than have as yet been discovered.

(3) According to this theory the greatest number of electrons which an atom can readily lose is the maximum positive valence number of the element. The method of positive rays indicate that there is no relation between these numbers. "The maximum number of charges carried by a multiply charged atom does not seem to be related to any chemical property of the atom such as its valency, but to depend mainly on the atomic weight."[2] The electron theory of valence indicates that the inert gases should give up electrons with great difficulty if at all. Helium readily loses two electrons, while the argon atom may carry one, two or three positive charges and that of krypton four or five. Positively and negatively charged atoms of hydrogen, oxygen, sulfur and chlorine have been found. Nitrogen and mercury atoms appear to be capable of acquiring a positive charge only,[3] the latter may lose any number from one to eight of electrons. Gases such as methane or carbon dioxide would be expected to yield carbon atoms carrying four positive or negative charges. Two appears to be the greatest number of charges which this atom is capable of acquiring.[4] According to the electron theory of valence, the carbon atom in carbon monoxide is positively charged, while the oxygen atom is negatively charged. The method of positive rays shows that when a molecule of this gas is dissociated in the vacuum tube the numbers of positively charged oxygen atoms and of positively charged carbon atoms are practically equal.[5]

The spectral method of analysis has yielded evidence regarding the existence of charged atoms, substantiating that obtained by the electromagnetic method.[6]

(4) In an equilibrium mixture of a gas and its dissociation products, new molecules of the gas are being continually formed while others are breaking up. The electron theory of valence predicts that such a mixture would contain more charged atoms or molecules than do stable gases at the same temperature and pressure. Conductivity measurements have failed to indicate any difference in the number of charged particles in these two classes of gases.[7]

[1] Thomson, "The Corpuscular Theory of Matter," p. 130, *et. seq.* (1907).

[2] *Idem.*, "Rays of Positive Electricity," p. 53.

[3] *Idem.*, *Proc. Roy. Soc.*, (*A*) **89**, 10 (1913).

[4] *Phil. Mag.*, **21**, 239 (1911).

[5] *Ibid.*, **24**, 249 (1912).

[6] Stark. *Physik Z.*, **14**, 961 (1913).

[7] *Phil. Mag.*, **24**, 250 (1912).

(5) One of the conclusions at which Kirkby arrived as a result of an investigation of the "Chemical Action of Electrical Discharge in Electrolytic Gas," was stated as follows: "The atoms of oxygen, when separated, are not charged electrically. This is proved by experiments independently of theory. Hence the atom of oxygen is not bound in a molecule of water vapor by electrostatic force."[1] Subsequent experiments by Kirkby and Marsh[2] on the explosion of azoimide between charged plates leads to a similar conclusion.

(6) In order for the atoms in a molecule to be held together by electrical forces it is not necessary that it be assumed that an electron has moved from one atom to another. Thomson has considered a distribution of electrons within the outer sphere of the atom which accounts for two neutral atoms being held together.[3] Stark, without employing the assumption that a chemical bond involves the transfer of an electron from one atom to another, has developed[4] a system by which the atoms of a molecule may be held together by means of electrical forces. Bohr,[5] assuming the structure which Rutherford[6] has proposed for the atom, showed that two atoms may be attracted to one another by electrical forces even though both are electrically neutral as a whole.[7] Such an electrical attraction between atoms involving no movement of an electron from one atom to another supports the idea of non-polar valences developed by Bray and Branch[8] and Lewis.[9] However, these authors consider polar valences also. Some of the difficulties which this dualistic view of valence presents have been pointed out by Falk and Nelson[10] and by W. A. Noyes.[11]

It will thus be seen that on the whole the phenomena of physics are opposed to the view that in the molecule the atoms are charged with respect to one another, and to the theory of valence developed on this assumption. Chemistry contributes the most satisfactory evidence in its favor. It explains in a simple and clear manner certain reactions, particularly the oxidation and reduction of electrolytes in solution. This is sufficient justification for its application to such reactions. The fact that electrolytes dissociate in solution into oppositely charged ions is not, however, conclusive evidence that in the molecule the atoms or groups of atoms are electrically charged with respect to one another. Ionization may consist essentially in the passage of an electron from one atom or group to another, these then separate from one another forming the ions. The ease with which this movement of the electron takes place depends upon the nature both of the substance and of the solvent. The distinction which is drawn between electrolytes and non-electrolytes is largely based upon the extent to which the substance is influenced by its environment. In the pure state as solid, liquid or gas, the molecule of an electrolyte differs but little in its behavior from that of other substances.

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[1] *Proc. Roy. Soc.*, (*A*) **85**, 151 (1911).

[2] *Ibid.*, **88**, 90 (1913).

[3] *Engineering*, **95**, 329 (1913).

[4] *Jahrb. Rad. Elektr*., **9**, 15 (1912); *Z. Electrochem.*, **19**, 862 (1913), Prinzipien der Atomdynamik (1910), Hirzel, Leipzig.

[5] *Phil. Mag.*, **26**, 857 (1913).

[6] *Ibid.*, **21**, 669 (1911).

[7] Recently, additional support has been lent to this "non-polar" view of the mechanism of the combination of atoms to form molecules. In November, 1913, when Bohr calculated on the above assumptions that the heat of combination of hydrogen atoms to form hydrogen molecules was 60,000 calories per gram molecule, the accepted experimental value was 130,000 calories. Since then Langmuir (*Phil. Mag.*, **27**, 188 (1914)) has published the results of further experiments which give the value 76,000 calories.

[8] THIS JOURNAL, **35**, 1440 (1913).

[9] *Ibid.*, **35**, 1448 (1913).

[10] *Ibid.*, **36**, 209 (1914).

[11] *Ibid.*, **36**, 214 (1914).

Nelson, Beans and Falk have given a general classification of reactions on the basis of the electron theory of valence. "In every reaction; I, If the algebraic sum of the positive and negative charges on a definite atom of the molecule changes; either A, the number of corpuscles on the atom increases; or B, the number of corpuscles on the atom decreases; II, If the algebraic sum of the positive and negative charges on the atom remains constant; either A, the arithmetrical sum changes; or B, the arithmetrical sum remains constant. Applied to chemical reactions, IA includes reduction reactions, IB adduction reactions, IIA onium compound formation, IIB metatheses in which none of the changes IA, IB or IIA takes place. Stated. slightly differently, the classification includes reactions involving reduction, oxidation, onium compound formation, and simple replacement or rearrangement."[1] These authors have discussed these types of reactions and have explained the electronic changes which are involved in each of these various classes.

It would apparently be impossible to discover or even imagine any reaction which could not be classified and explained on such a basis. Thus, suppose some entirely new type of reaction were discovered. Then, on the basis of this theory, if the algebraic sum of the positive and negative charges on a definite atom changes during the reaction, by definition the reaction is one of oxidation-reduction and as such is explainable. If, on the other hand, the algebraic sum of the charges on a definite atom remain the same, the reaction is by definition an "onium" compound formation or a metatheses, which also may be explained by the electron theory of valence. From the nature of the definitions and the breadth of the classification, the discussion has been removed from dependence upon experimental data. In other words, a discussion on the basis of such a classification of the electronic changes taking place during reactions can neither support or refute the theory. On the other hand, if the assumptions of the theory be granted, a useful method of classifying reactions may be derived.

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[1] THIS JOURNAL, 35, 1815 (1913).

A similar remark applies to the application of the theory to the structure of molecules. The electron theory has been applied by various authors to the structure of such chemical substances as chlorine, hydrogen peroxide, ammonium chloride, etc. If molecules such as these can be satisfactorily explained, it would seem that every conceivable molecule could be explained on the same basis. Apparently some new line of attack, such as that recently undertaken by W. A. Noyes,[1] must be looked to for any decisive argument of a chemical nature for or against the theory.

The classification and relation of compounds and reactions, which has resulted from the application of the electron theory of valence, has been of value. The part played by its fundamental assumption has been largely a means of relating phenomena and the actual movement of the electron is not necessarily involved in the conclusion. That is, it is possible that some other assumption involving the ideas lately proposed by Thomson or those developed by Stark or by Bohr would lead to a similar classification of compounds and reactions.

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URBANA, ILL.

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

AN APPARATUS FOR THE MEASUREMENT OF VAPOR PRESSURES BY THE DYNAMIC METHOD AND DETERMINATIONS OF THE VAPOR PRESSURE OF WATER AT 24.97°.[2]

BY I H DERBY, F. DANIELS AND F. C. GUTSCHE.

Received March 19, 1914

It has been generally conceded that the dynamic, or "air bubbling," methods for determining vapor pressures of liquids offer considerable promise, but, owing to the more or less cumbersome and complicated apparatus required by such processes, these methods have not been utilized save in a few instances. Regnault[3] in 1845 was seemingly the first to use the dynamic method. His procedure consisted in passing a known volume of air over a moist sponge and through moist silk screens, and weighing the water vaporized, thus obtaining values for the vapor pressure of water which agreed very closely with results obtained by static methods. This method of Regnault's was subsequently used with various modifications and with varying degrees of success by Tamman,[1] Walker,[2] Will and Bredig,[3] Linebarger,[4] Orndorff and Carrell,[5] Perman,[6] Carveth and Fowler,[7] Kahlenberg,[8] Earl of Berkeley and Hartley,[9] Lincoln and Klein,[10] and Krauskopf.[11]

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[1] THIS JOURNAL, 35, 767 (1913).

[2] Presented at the annual meeting of the American Chemical Society, December, 1910

[3] *Ann chim. phys*, 3, 15, 129 (1845).

Linebarger used a saturator of five Liebig bulbs through which a known volume of air was forced. The vapors were chemically analyzed and the partial pressures of a variety of mixtures of miscible liquids thereby determined. Perman used a Liebig bulb with four large compartments and obtained some very satisfactory results. Kahlenberg devised a saturator consisting of a large glass vessel partly filled with the liquid and shaken laterally in a thermostat, air being drawn through by a large aspirator. This device was used successfully by Lincoln and Klein and by Krauskopf. In connection with some work being done in this laboratory it became necessary to determine the vapor composition and partial pressures of alcohol and water mixtures, and with this end in view an apparatus, embodying several new features, was designed; and its description together with evidence of its efficiency as shown by measurements of the vapor pressure of water at 24.97°, is here presented.

The apparatus in its final form is shown in outline in Fig. 1. With the exception of the drying towers and the aspirating bulbs, the whole apparatus was placed in a large electrically heated and regulated water thermostat (100 gallons), in which the temperature could be maintained constant within a few thousandths of a degree. The two large towers for purifying and drying the air were filled (*R*) with soda lime and (*T*) with pieces of pumice stone rolled in phosphorus pentoxide. These were connected with the saturator, Figs. 1 and 2, which is the unique feature of the apparatus.

In the following experiments, and in determinations of vapor pressure and vapor composition which will appear in a later paper, the saturator consisted of two three-inch, thrice tubulated bulbs, filled with glass pearls of about 4 mm. diameter. These bulbs were connected with each other and with the exterior, as shown in Fig. 2, and were held rigidly in position by a wooden frame, (not shown in figure) built in halves, to permit of easy removal and assembling of the parts. A small electric motor, belted to a pulley at one end of the wooden frame, served to rotate it with the contained bulbs. The glass tubes *K*, functioned as axles for the bulbs and rotated in journals of short glass tubing which were supported by clamps. The tubulatures *M*, closed by rubber stoppers, were for the filling and emptying of the bulbs. To retain the pearls in place and prevent the liquid from draining into the connecting tubes, thus cutting off the air passage, their ends were protected by perforated platinum cones *N*; and as the liquid ran down the side of the bulb, it was caught by the cone and drained toward the tip, while any liquid which might get back of the cone was prevented from entering the conducting tubes by flanging the ends and extending them a short distance through the stoppers, not far enough, however, to touch the cones. To form air-tight connections with the rest of the apparatus while still allowing horizontal rotation of the saturator, use was made of mercury seals *S*, and thick-walled soft rubber tubing *L*, bent down through an angle of 90 degrees. This latter connected the tubes *K* with short pieces of glass tubing, *Q*, fitting loosely over the glass tubing from the drying towers and absorption tube and rotating easily on them as axes. These tubes *Q* were fitted with jacketing tubes *P* which formed a tight joint at the upper end but had the annular aperture left open below. The annular space thus formed was coated with paraffine and when connected was half filled with mercury. This device not only doubled the distance which water must pass over to get from the thermostat into the bulbs, but also interposed a trap formed by the air filled

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[1] *Wied. Ann.*, **33**, 322 (1888).

[2] *Z. physik. Chem.*, **2**, 602 (1888).

[3] *Ber.*, **22**, 1084 (1889).

[4] THIS JOURNAL, **17**, 615 (1895).

[5] *J. Phys. Chem.*, **1**, 753 (1897).

[6] *Proc. Roy. Soc. London*, **72**, 72 (1903).

[7] *J. Phys. Chem.*, **8**, 313 (1904).

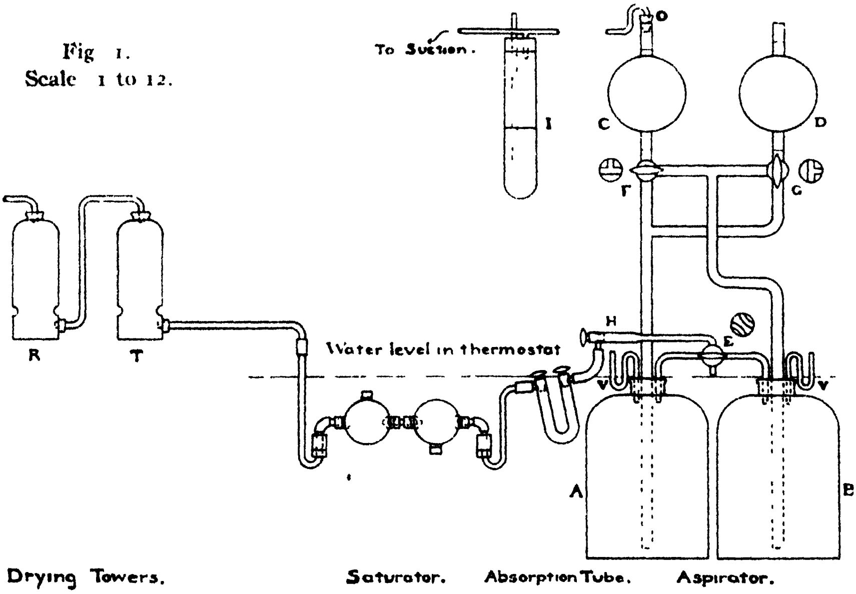
[8] *Science*, **22**, 74 (1905).

[9] *Proc. Roy. Soc. London*, **77**, 156 (1906).

[10] *J. Phys. Chem.*, **11**, 318 (1907)

[11] *Ibid.*, **14**, 489 (1910).

Fig 1.
Scale 1 to 12.



annular space above the mercury. This arrangement, adopted after the unsatisfactory trial of several other schemes, proved effectual in preventing entrance of water to the saturator by capillary action. It should be further noted that the terminal tubes *Y* of the saturator, where they enter the mercury seals, must extend 2 or 3 cm. above the mercury in the cup, to prevent the suction applied in the aspirators from drawing mercury into the tubes. The saturator, including the mercury seals, was supported by a single ringstand, thus enabling transference independently of the rest of the apparatus.

The absorption tubes employed were five-inch glass stoppered tubes, (Schwarz design), and were filled with granulated pumice stone which had been coated with phosphorus pentoxide. A rubber cap was fitted over the stopcock through which the saturated air entered the absorption tube, so that it might be kept dry because of difficulty in drying the groove around the stopcock. The other stopcock was not submerged. The absorption tube was connected in by means of thick walled flexible rubber tubing, thus allowing easy removal and replacement for the purpose of weighing. Between the absorption tube and the aspirator was placed a small drying tube *H*, also charged with phosphorus pentoxide to prevent back diffusion of water vapor.

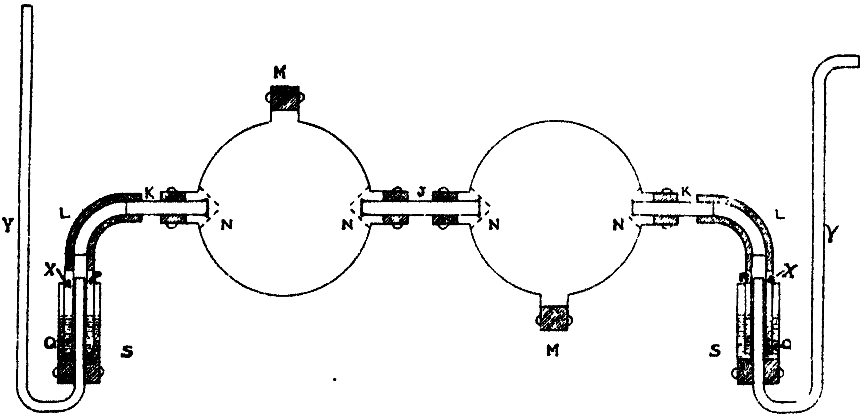


Fig. 2.
Scale 2 to 7.

The aspirator consisted of two calibrated bulbs, *C* and *D*, connecting interchangeably, through the three-way cocks *F* and *G*, with the two eight-liter bottles *A* and *B*. By this arrangement one bottle served as aspirator while the other received the drain from the bulbs. In this way the aspiration became practically a continuous process independent of the size of the aspirating bottles *A*, *B*, since one bulb drained while the other was filling. These two bulbs were calibrated to take up 1135 cc. each between the etched lines *cc dd*, at a temperature of 25°, when allowed to drain for ninety seconds. Each bottle was fitted with a manometer *V*, and a four-way stopcock *E* placed between the bottles made it possible to connect either one of them with the air and the other with the saturating and absorbing train. A rubber stopper *O*, fitted with a glass tube, was connected with the water air pump through a mercury pressure regulator *I*, designed to preserve any desired constant exhaustion, thus regulating the speed of aspiration. The connection *O* could be shifted from one aspirating bulb to the other.

This disposition of the apparatus keeps the aspirator water at the temperature of the thermostat, within narrow limits, thus making the temperature of the aspirated air and the vapor pressure of water, over which it collects, definitely fixed values.

In conducting an experiment the saturation bulbs, filled with glass pearls, were charged with the liquid to be investigated to a level a few millimeters (2 or 3) below the lower edges of the cones. If too much liquid be added any slight tilt of the apparatus throws it into the connecting tubes. The saturator was then placed in the thermostat and connections made with the purifying towers at one end and the aspirator, through the carefully weighed absorption tube, at the other, as shown diagramatically in Fig. 1. The absorption tubes charged with the phosphorus pentoxide were counterpoised in pairs and the members of a pair were then used alternately. This arrangement was adopted to eliminate, as far as possible, errors due to changes in barometric pressure, temperature and humidity. Weights were taken to the nearest 0.1 mg. although the scale was sensitive to 0.03 mg. It was found necessary to allow the tube used for the absorption to stand nearly an hour before a constant weight was obtained. Trouble was at first experienced due to condensation of vapor in the side arm when the absorption tube was first connected. This difficulty was avoided by slightly warming the tube before making connections. After assembling and connecting the apparatus, 40 to 50 minutes were allowed, in order that the saturator and the aspirator might come to the temperature of the thermostat, previous to the first determination. For subsequent determinations no waiting was necessary, provided the saturator remained continuously immersed. When temperature equilibrium had been attained the saturator was first set rotating at a rate of thirty or forty turns per minute. The aspiration was then started. When sufficient air had been aspirated, in the experiments on water of 25°, usually 8 to 10 liters, a few seconds were allowed to elapse before closing the stopcocks, in order to permit establishment of barometric pressure throughout the apparatus. The water manometers *V*, Fig. 1, showed conclusively when this condition obtained. The absorption tube could then be closed, disconnected and prepared for weighing and one of another pair substituted for a new run. With three pairs of tubes a number of determinations may be carried out in a single day. At the conclusion of an experiment only three observations are necessary; first, the total volume of saturated air aspirated and measured by the water passed through the calibrated bulbs *CD*; second, the barometric pressure; third, the gain in weight of the absorption tube. In our experiments the time actually taken for the aspiration was also recorded, mainly for the purpose of comparison.

The formula used for calculating the vapor pressure is essentially the same as that employed by Tamman,[1] except that it was found unnecessary to introduce any corrections for change of volume of the aspirating bulbs, since they were calibrated and used at the one temperature, namely, 25° C. The symbols employed and their significance together with the numerical constants used in developing the formula are as follows:

P. Corrected barometer pressure.

V. Volume of saturated air measured by aspirator.

$P_0 = 760.0$. Standard barometer pressure.

$t = 24.97°$. Temperature of aspirator.

$p_3 = 23.7$ mm. Vapor pressure of water in aspirator at temperature t.

$a = 0.003571$. Coefficient of expansion of air.

$d = 0.0012728$. The density of dry air at 0°, 760 mm.

$V_0 = 22400$ cc. The gram molecular volume of air at 0°, 760.

M. Hypothetical molecular weight of air from the gram molecular volume of air, as determined from the gram molecular volumes of its constituents.

$M_1 = 18.015$. .Molecular weight of water vapor calculated from the atomic weights.

p. Partial pressure of air in mm. in saturation bulbs when equilibrium is established.

p_1. Partial pressure of water vapor in mm. in saturation bulbs when equilibrium is established.

V_1. Volume of air and saturated water vapor in cc. formed in saturation bulbs during an experiment.

w. Weight in g. of air aspirated.

w_1. Weight in g. of water vapor determined by weighing.

Using the symbols as listed and assuming the gas laws to hold, three fundamental equations are readily formulated:

$$(1). \qquad P = p + p_1.$$

$$(2). \qquad PV_1 = \frac{w}{M} RT.$$

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[1] *Loc. cit.*

(3). $$p_1V_1 = \frac{w_1}{M_1} RT.$$

Solving (2) and (3) for V_1, equating and substituting for p its equivalent value from (1), then solving for p_1 gives

(4). $$p_1 = \frac{P}{1 + \frac{M_1 w'}{M w_1}}.$$

We may place

(5). $$M = dV_0.$$

The weight of w' is readily obtained from the general gas law relation involving that term

(6). $$(P - p_3)V = \frac{w'}{dP_0} P_0V_0(1 + at).$$

Which solved for w' gives

(7). $$w' = \frac{(P - p_3)Vd}{P_0(1 + at)}.$$

Substituting in (4) the equivalent of M from (5) and w from (7) gives the general formula

(8). $$p_1 = \frac{P}{1 + \frac{(P - p_3)VM_1}{w_1(1 + at)P_0V_0}}.$$

Substituting numerical constants gives

(9). $$p_1 = \frac{P}{1 + \frac{(P - p_3)V\ 18.015}{w_1(1 + 0.003671t)\ 760 \times 0.22400}}.$$

The value of 18.015 760 × 0.22400 for all experiments with water or water solutions is constant and may be reduced to one term.

$$\frac{18.015}{760 \times 0.22400} = 0.0000010582.$$

(log. 0.0000010582 = 4.02457 10) which substituted in (9) gives

(10). $$p_1 = \frac{P}{1 + \frac{(P - p_3)V\ 0.0000010582}{w_1(1 + 0.003671t)}}.$$

the formula used for calculating the results of Gutsche's experiments.

If, as was the case in all subsequent experiments, t is a constant (in this case 24.97) then $(1 + 0.003671t)$ becomes a constant and

$$\frac{18.015}{(1 + 0.003671 \times 24.97)\ 760 \times 0.22400} = 0.0000009694.$$

(log. 0.0000009694 = 3.98649 - - 10) which may be used in all experiments, giving for the formula

$$p_1 = \frac{P}{1 + \frac{(P - p_1)V\ 0.0000009696}{w_1}}. \qquad (11).$$

Further, V may be kept constant in any series of determinations, thus still further simplifying the calculations. This was done in the two series of determinations listed in Tables II and III.

To test the efficiency of the saturating and absorbing parts of the apparatus, a number of determinations were made on the vapor pressure of water at 24.97°. Table I shows the first results obtained by Gutsche on water, and a single determination with absolute ethyl alcohol, prepared by drying over lime and distillation from sodium. In these experiments the aspirating bottles were, as is customary, outside of the thermostat. They were calibrated for total volume and operated by a syphon. The significance of each column is indicated by the symbol above it the meaning of which has been given in the course of developing the formula.

TABLE I.

No. of expt.	t.	V.	P.	w_1.	p_1.	Time of aspiration in minutes.
1	21.55	8043	736.7	0.1958	23.55	10
2	20.30	8120	739.0	0.1974	23.60	14
3	20.80	8400	738.9	0.2015	23.30	35
4	19.90	8121	737.7	0.1969	23.50	11
		Alcohol.				
				w_2.[1]	p_2.[1]	
5	19.40	8456	738.8	1.3692	58.47	21

TABLE II.

No. of expt.	V.	P.	w_1.	p_1.	Time of aspiration in minutes.
1	8000	745.8	0.1841	23.73	11
2	8000	734.4	0.1819	23.45	29
3	8000	737.1	0.1829	23.58	47
4	8000	743.4	0.1844	23.76	11
5	8000	734.3	0.1834	23.65	21
6	8000	736.4	0.1824	23.52	13
7	8000	736.4	0.1840	23.72	12
8	8000	738.7	0.1833	23.63	12
9	8000	735.0	0.1844	23.77	11
10	8000	735.0	0.1833	23.63	43
11	7992	730.6	0.1829	23.60	25
12	8000	738.8	0.1842	23.75	13
13	8000	738.8	0.1845	23.73	13
14	8000	731.7	0.1846	23.80	37
			Average,	23.67	

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[1] w_2 and p_2 stand for the weight of alcohol evaporated and the calculated vapor pressure, respectively. Phosphorus pentoxide was used for absorbing the alcohol vapor. The absorption was complete and nearly as vigorous and rapid as with water,

The next experiments, Table II, were performed by Daniels and were made with the aspirating bottles submerged in the thermostat; but the water was drawn off by a syphon into standard liter flasks and a measure of the volume of air aspirated thus obtained.

In addition to the errors of volume introduced, because of the clumsy method of aspiration, a slow leak was later detected in one of the rubber connections which may account for the lower values, especially of the longer time intervals.

In Table III are the more accurate results, also obtained by Daniels with the final form of apparatus as detailed above. All rubber connections were made of heavy walled tubing and wired, and the apparatus was tested before each determination by closing the first stopcock of the absorption tube and withdrawing some water from the aspirator. The manometer rose and was observed for several minutes, and if the level in the manometer did not change, the apparatus must be air-tight.

TABLE III.—VAPOR PRESSURE OF WATER AT 24.97°.

No. of expt.	V.	P	w_1	p_1.	Time in minutes for expt.
1.	10,215	734.9	0.2344	23.67	20
2.	10,215	749.0	0.2348	23.71	15
3.	10,215	745.1	0.2349	23.72	15
4.	10,215	746.2	0.2350	23.73	20
5.	10,215	736.8	0.2345	23.68	14
6.	10,215	742.5	0.2345	23.68	20
7.	10,215	740.7	0.2349	23.72	12
8.	10,215	741.5	0.2348	23.71	23
			Average,	23.70	
9[1].	10,215	741.5	0.2352	23.75	40

The temperature of the thermostat for all the experiments (Tables I, II and III) was maintained at 25.00 ± 0.01 as indicated on a standard thermometer divided into 0.1° and easily read to within 0.01°. This thermometer had been calibrated by the Reichsanstalt in 1903 and was at that time without correction at 25.00°.

In the summer of 1911, following the above work which was carried out in 1910 to 1911, the thermometer was recalibrated by the U. S. Bureau of Standards and found to have a correction of —0.035°. The true temperature of the experiments then was 24.97° instead of 25.00°. After receiving the new calibration the thermostat was brought to exactly 25.00° and one more determination was made with the result recorded. By interpolation from the variations of pressure per degree from 24–26°, 0.035° C. corresponds to a change in the vapor pressure of water of 0.05

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[1] Temperature, 25.00°.

mm., which added to the vapor pressure values listed in Tables I, II and III, gives the values for 25.00°. It is significant, but can be taken only as a coincidence, that 0.05 mm. added to the average of the determinations 1 to 8 in Table III give the values found in the single determinations at 25.00°. Table IV shows a comparison of the results obtained in this work with values given by several other observers at the same temperatures.

Observer	Method	Pressure.
Regnault[1]	Dynamic	23.55
Lincoln and Klein[1]	Dynamic	23.76
Holborn and Henning[2]	Static	23.69
Eckholm[3]	Interpolation formula	23.79
Scheel and Heuse[4]	Static	23.76
Krauskopf[1]	Dynamic	23.71
Derby and Daniels....	Dynamic	23.75

The limits of error of observation allowable are fairly large, considering the weight of water evaporated in each experiment. A variation of 0.01 mm. pressure in the above results corresponds to a weighing error of 0.1 mg.; a volume error in measuring the aspirated air of 5 cc.; a temperature fluctuation of 0.007°, or an error of 1 mm. in the barometer reading. The extreme variation in the final, most reliable, series of determinations is seen to be 0.06 mm. which is a smaller variation than is found in the results of most other users of the dynamic method. This agreement is considered especially satisfactory, since most observers have used much larger volumes of air, and evaporated larger quantities of water. As may be noted, the volume of water evaporated is equivalent to not more than five or six drops from an ordinary buret.

The speed at which air becomes saturated with vapor has been considered by previous investigators and while several believed this to be a slow process and consumed days for a single determination, Lincoln and Klein[1] proved that a rate of at least 16 liters per hour was not too fast, and Regnault[1] stated that 25 liters per hour gave satisfactory results. The above experiments go further and prove that air becomes completely saturated with water vapor in the saturator if run through as rapidly as 50 liters per hour (Determination No. 7, Table III) and this is probably far from the maximum speed with the above described saturator. This establishes the efficiency of the saturator as well as that of the absorption tube. It is evident, then, that a determination may be made in a very short time, the most time being consumed in waiting for the absorption tubes

[1] *Loc. cit.*

[2] *Ann. d. Phys.*, **26**, 865 (1908); calculated from results above 50°.

[3] *Arkiv. Math. Astr. Phys.*, **4**, 29 (1908).

[4] *Ann. d. Phys.*, [4] **31**, 715 (1910).

to come to constant weight, and this delay is avoided, as indicated, by having two or three sets of tubes.

An important feature of the apparatus lies in the fact that barometric pressure is maintained throughout, except that a slight reduction of pressure is caused by the resistance of the whole train to the passage of the air during aspiration. This effect is negligible in the saturators where equilibrium is established. This is a distinct advantage over most previous apparatus, in which air has been bubbled through the liquid for saturation or through sulfuric acid in the absorption tube; for any error or correction due to the hydrostatic pressure of the liquid is avoided.

In working with mixtures or solutions, the vapor pressure is not affected by change in concentration or cooling from evaporation, because the volume of the solution is large relative to the amount evaporated, and any slight lowering of the vapor pressure due to the above causes in the first bulb is corrected for by the passage through the fresh liquid in the second bulb in which little evaporation takes place and, hence, a negligible cooling and change of concentration occur. The rotation, too, prevents the formation of layers of different concentrations, insures a thorough mixing of the liquid and exposes a large, continuously fresh surface from which evaporation takes place. In addition to the above mentioned advantages, the apparatus, with the exception of the large thermostat, may be cheaply and simply made from materials available in any laboratory.

The chief disadvantage of the apparatus lies in the fact that for a determination of each new liquid the saturator must be taken apart and the pearls removed, washed and dried, but with two saturators this delay is reduced to a minimum. A little practice is necessary, also, to operate the stopcocks accurately and rapidly. The method, too, is hardly suitable for use with liquids of extremely high vapor pressures unless the absorbent is changed frequently.

The apparatus as described is suitable for the measurement of vapor pressures not only of simple liquids but also of solutions and liquid mixtures, and has been applied, as previously stated, for the determination of the vapor composition and partial pressures of water ethyl alcohol mixtures. These results are soon to appear. The apparatus should be further admirably adapted to the accurate determination of vapor pressure of saturated solutions and solubility, for in place of the glass pearls the saturator might be filled with the crystallized salt, the liquid added being a nearly saturated solution.

With the rubber connections the applications of the apparatus are limited to substances which do not affect rubber. The recent discovery,[1] however, of a method by which any substance may be metallic-plated by nearly any metal might allow of the gold or silver plating of the interior of all connections when the apparatus might be used for anything not attacking glass.

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[1] Schoop.

Summary.

A very satisfactory apparatus for measuring vapor pressures has been devised and tested, of which the saturator has proved extremely efficient, and the aspirator accurate and convenient.

Experiments show that air may be completely saturated with water vapor at the rate of at least 50 liters an hour in the above described saturator.

The efficiency of phosphorus pentoxide as a very rapid absorbing agent is further confirmed.

One determination of the vapor pressure of absolute ethyl alcohol at 25° has been made and a pressure of 58.47 mm. found.

The value of 23.70 mm. for the vapor pressure of water at 24.97° and 23.75 mm. at 25.00° has been obtained by this method.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE POTENTIAL OF THE COPPER ELECTRODE AND THE ACTIVITY OF BIVALENT IONS.

BY GILBERT N LEWIS AND WILLIAM N LACEY

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The determination of the E. M. F. of cells involving bivalent or multivalent ions presents no greater difficulties than those which are met in the simple case in which only univalent ions are concerned. The interpretation, however, of the measurements of cells of the former type is by no means easy. If ternary salts, such as $CuCl_2$ or K_2SO_4, are employed, we have at present no means of determining the concentration of intermediate ions such as $CuCl^+$ and KSO_4^-, which may be, and probably are, present in considerable amount. Aside from this obstacle, there are at present no adequate data with which to calculate the degree of dissociation or the activity of the ions in salts of higher type than the uni-univalent. For such a calculation it is necessary to determine the free energy of dilution either by measurements of electromotive force, or of freezing point, or of some other property of the solution which is related thermodynamically to these.

The Free Energy of Dilution of Copper Sulfate.—The electromotive forces of the cells Cu, $CuSO_4$, 0.05 M, Hg_2SO_4, Hg, and Cu, $CuSO_4$, 0.005 M, Hg_2SO_4, Hg were first measured. Each cell consisted of two half-cells of the customary form. The copper electrode was prepared by surrounding a copper-plated platinum wire situated at the bottom of the electrode vessel with finely divided copper. This copper was at first obtained by the method of Richards[1] in which a current of concentrated copper sulfate solution passes first through a hot tube containing metallic copper and then through a cold tube where copper is reprecipitated. The metal thus obtained was found, however, to be less satisfactory than that prepared by electrolyzing tenth normal copper sulfate solution at sufficient current density to bring down a spongy nonadherent deposit.[2] The spongy metal was allowed to stand in a solution of copper sulfate, of the concentration to be used in the cell, and was then carefully washed and transferred to the electrode vessel. As in the case of silver, the metal thus prepared seems to be free from the surface strains which characterize electrodes plated with a coherent film. Such electrodes, which have previously been used in the determination of the potential of the copper electrode, are entirely unreliable and will often differ in potential among themselves by a centivolt. When the current density is such as to cause the deposited film to break and to develop as a tree or sponge, the surface strains are, doubtless, to a large extent relieved, and, on standing in contact with the solution, rapid local action, due to the large surface exposed, will remove any portions of the metal which might still have a high potential.

The copper sulfate was prepared from the commercial C. P. product by two recrystallizations. In order that the equilibrium between copper and cupric and cuprous ion might be as nearly as possible established in advance, the solution to be used in the electrode chamber was shaken from ten to twenty hours with finely divided copper in a thermostat at 25°. The half-electrodes were then set up and their electromotive force measured against one another and against the mercurous sulfate electrodes.

The latter electrodes were prepared from pure mercury and from mercurous sulfate obtained by the Hulett method.[3] These substances were washed by shaking them up together with the copper sulfate solution, decanting the solution, and repeating this process as in the preparation of normal calomel electrodes. These electrodes proved to be admirably constant both in tenth and hundredth normal solutions and reproducible to 0.0001 V.

The copper electrodes, on the other hand, showed a greater variability. In the final experiments nine 0.05 M electrodes showed an average deviation from the mean of 0.00023 V. and fifteen 0.005 M electrodes an average deviation of 0.00036 V. Oxidation in the copper electrodes, owing to the presence of air, seemed to play no important role, as shown by the fact that similar results were obtained with electrodes in the complete absence of oxygen. The method of preparation of the copper electrode suggested the possibility that occluded hydrogen might be taking part in the electrode process, but if this were the case the potential would vary with the concentration of H^+, whereas experiments showed that the presence of 0.001*N* sulfuric acid in the copper sulfate solution made no change in the electromotive force.

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[1] *Z. physik. Chem.*, **32**, 321 (1900).

[2] For the preparation of a similar silver electrode see Lewis, THIS JOURNAL, **28**, 158 (1906).

[3] *Phys. Rev.*, **32**, 257 (1911).

The mean values for the two cells[1] were

$$\text{Cu, CuSO}_4\ 0.05\ \text{M, Hg}_2\text{SO}_4\text{, Hg; } \mathbf{E} = 0.3928\ \text{V.}$$

$$\text{Cu, CuSO}_4\ 0.005\ \text{M, Hg}_2\text{SO}_4\text{, Hg; } \mathbf{E} = 0.4226\ \text{V.}$$

The difference between these two values, 0.0298 V., is the electromotive force corresponding to the free energy of dilution of copper sulfate from 0.05 M to 0.005 M. Now this difference can also be calculated from the conductance values of $CuSO_4$, assuming Kohlrausch's law and the validity of the laws of perfect solution, by the formula

$$\mathbf{E} = \frac{RT}{2F} \ln \left(\frac{c_1\gamma_1}{c_2\gamma_2}\right)^2$$

where γ is the value of λ/λ_0 at the concentration c. From the conductance tables given by Noyes and Falk,[2] γ (0.05 M) = 0.396, γ (0.005 M) = 0.629, and $\mathbf{E}$ = 0.0472 V., which differs from the measured value by 0.0174 V. It is evident, therefore, that the assumptions upon which the above formulae are based are far less accurate in this case than in the case of the simple uni-univalent salts.

Another method of calculating the free energy of dilution which, like the e. m. f. method, rests upon no questionable assumption, is the one in which the freezing point data are used. Unfortunately, few freezing-point determinations have been sufficiently accurate to justify their use in such a calculation. In the case of copper sulfate, however, the measurements of Hausrath[3] and Bedford[4] between 0.0002 M and 0.03 M seem entirely reliable. Between 0.03 M and 0.1 M no values are available except one obtained by Jones, Getman and Bassett[5] and one by Raoult.[6] We have nevertheless attempted to extrapolate the curve through the points of Hausrath and Bedford up to 0.05 M.[7]

This curve was then employed to determine the free energy of dilution

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[1] All measurements were made in an oil thermostat at 25 00°.

[2] THIS JOURNAL, 34, 454 (1912).

[3] *Ann. Phys.*, [4] 9, 544 (1902).

[4] *Proc. Roy. Soc.*, 83A, 459 (1910).

[5] Landolt-Börnstein-Roth, 4 Aufl., 809.

[6] *Z. physik. Chem.*, 2, 489 (1888).

[7] The freezing-point curve that we have used passes through the points given in the following table. This table also contains similar data for H_2SO_4 to be used later:

Mol. conc.		0.0005	0.001	0.002	0.005	0.01	0.02	0.03	0.05
Mol. F. P. Lowering	$CuSO_4$	3.23	3.15	3.04	2.87	2.70	2.50	2.41	2.34
	Hg_2SO_4	5.34	5.26	5.15	4.94	4.71	4.46	4.32	4.16

of $CuSO_4$ by means of the formula given by Lewis,[1] $\int d\overline{F}_1 = 292.2 \int (1/c)\, d\theta$, where $\overline{F}_1$ is the partial molal free energy of the solute in calories, and c is the concentration in mols per thousand grams of water, at which the freezing-point lowering is θ. The integration gives for the free energy of dilution between 0.05 M and 0.005 M, 1590 calories, and between 0.005 M and 0.0005 M, 1949 calories.

The first of these values when multiplied by the mechanical equivalent of heat and divided by twice the Faraday equivalent gives 0.0344 V., which should be identical[2] with the difference between the E. M. F. of the above cell with 0.05 M and 0.005 M $CuSO_4$, namely, 0.0298 V. The difference of 0.0046 V. is probably due to our choice of too high values of the freezing-point lowering at concentrations above 0.03 M, where it was necessary to extrapolate from the experiments of Hausrath and Bedford.

The second value, 1949 cal., corresponding to 0.0422 V., enables us to calculate from the E. M. F. at 0.005 M the E. M. F. at 0.0005 M, namely,

$$Cu,\ CuSO_4\ 0.0005\ M,\ Hg_2SO_4,\ Hg;\ \mathbf{E} = 0.4648\ V.$$

Now we will assume that at this high dilution the degree of dissociation is measured accurately by the conductivity, and the activities of the ions are proportional to the concentrations so measured. We may then write the equation,[3]

$$\mathbf{E} = \mathbf{E}^\circ - (RT/2F) \ln (Cu^{++})(SO_4^{--}).$$

Now from $\mathbf{E} = 0.4648$ V., taking the degree of dissociation in 0.0005 M as 0.862, we find $\mathbf{E}^\circ = 0.2658$ V. This is the electromotive force which would be exhibited by such a cell with Cu^{++} and SO_4^{--} each at (hypothetical) molal concentration. $\mathbf{E}^\circ$ is the difference between the two *normal* electrode potentials Cu, Cu^{++} and Hg, Hg_2SO_4, SO_4^{--}.

The Free Energy of Dilution of Sulfuric Acid.—Cells of the form H_2, H_2SO_4, Hg_2SO_4, Hg were also investigated. The Hg_2SO_4 electrodes were made up as before. The hydrogen electrode was of the form employed in other investigations in this laboratory and will be described in another place. Both electrodes showed excellent constancy and reproducibility and the following results, representing in each case the mean of several determinations, may be considered correct to 0.0001 V.:

$$H_2,\ H_2SO_4\ 0.05\ M,\ Hg_2SO_4,\ Hg;\ \mathbf{E} = 0.7545\ V.$$

$$H_2,\ H_2SO_4\ 0.005\ M,\ Hg_2SO_4,\ Hg;\ \mathbf{E} = 0.8160\ V.$$

In the case of a ternary electrolyte, which certainly dissociates in part into intermediate ions, conductivity data alone are insufficient for the calculation of the concentration of the various constituents, even when the principle of Kohlrausch is assumed. Noyes and Stewart[1] have attempted to determine the composition of solutions of sulfuric acid by combining the conductivity data, (*a*) with transference data, (*b*) with "isohydric" data. The results of their calculations of the molal concentrations of H^+, HSO_4^- and SO_4^{--} at concentrations 0.05 M and 0.005 M are given in the following table:

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[1] THIS JOURNAL, 34, 1635 (1912).

[2] The freezing-point data give the free energy values at about 0° and not at 25°, but the difference is smaller than the probable experimental error.

[3] For a discussion of these equations and the notation employed, see Lewis, THIS JOURNAL, 35, 23 (1913).

		H^+	HSO_4^-.	SO_4^{--}.
0.05 M	(*a*)	0.0625	0.0315	0.0155
	(*b*)	0.0585	0.0355	0.0115
0.005 M	(*a*)	0.0081	0.0017	0.0032
	(*b*)	0.00825	0.00155	0.00335

Assuming the activity of these ions to be proportional to their concentration we would have the equations,

$$E = E^\circ - (RT/2F) \ln (H^+)^2(SO_4^{--})$$

$$E' = E^{\circ\prime} - (RT/2F) \ln (H^+)(HSO_4^-)$$

From our measurements $E = E' = 0.7545$ V. at 0.05 M, and $E = E' = 0.8160$ V. at 0.005 M. Substituting these values and the concentrations from the table in the formulae we find at 0.05 M, $E^\circ = 0.6299$ V. (*a*) and 0.6243 V. (*b*); at 0.005 M, $E^\circ = 0.6186$ V. (*a*) and 0.6197 V. (*b*). The discrepancy between the values found at the two concentrations, amounting to 11 millivolts (*a*) and 5 millivolts (*b*), shows in this case also, either that very serious errors have been made in determining the concentration of the ions, or that the activities are far from proportional to the concentrations. The corresponding calculation of $E^{\circ\prime}$, involving only univalent ions, gives, as might be expected, more concordant results; thus at 0.05 M, $E^{\circ\prime} = 0.6745$ V. (*a*) and 0.6752 V. (*b*); while at 0.005 M, $E^{\circ\prime} = 0.6724$ V. (*a*) and 0.6714 V. (*b*).

The freezing-point data for sulfuric acid are far more numerous, but also less concordant, than those for copper sulfate. We have attempted, after plotting all the data, to construct the most probable curve between 0.05 M and 0.0005 M. Sample points of the curve have been given in one of the previous footnotes. From this curve we calculate for the electromotive force corresponding to the dilution from 0.05 M to 0.005 M, $E = 0.0613$ V., which agrees surprisingly well with the difference between the two E. M. F.'s measured above, namely, 0.0615 V. The similar calculation from 0.005 M to 0.0005 M gives 0.0731 V., so that we may calculate,

$$H_2, H_2SO_4\ 0.0005\ M, Hg_2SO_4, Hg;\ E = 0.8891\ V.$$

By a sort of extrapolation from the values given by Noyes and Stewart at higher concentrations we estimate that in 0.0005 M H_2SO_4 the concentrations of H^+ and SO_4^{--} are, respectively, 0.00097 M and 0.00047 M.

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[1] This Journal, 32, 1148 (1910).

Assuming now that at this high dilution the activities of the ions are proportional to the concentrations thus determined, we may as before write

$$\mathbf{E} = \mathbf{E}^\circ - (RT/2\mathbf{F}) \ln (H^+)^2(SO_4^{--}),$$

and substituting the numerical data we find $\mathbf{E}^\circ = 0.6127$ V. This is therefore the difference between the *normal* electrode potentials H_2, H^+ and Hg, Hg_2SO_4, SO_4^{--}.

The Potential of the Copper Electrode.—In the two preceding sections we have calculated for two cells the normal E. M. F., that is, the E. M. F. when the ion concentrations are (hypothetical) molal, namely,

$$Cu, Cu^{++} \parallel SO_4^{--}, Hg_2SO_4, Hg;\ \mathbf{E}^\circ = 0.2658\ V.$$

$$H_2, H^+ \parallel SO_4^{--}, Hg_2SO_4, Hg;\ \mathbf{E}^\circ = 0.6127\ V.$$

By subtracting we therefore find,

$$Cu, Cu^{++} \parallel H^+, H_2;\ \mathbf{E}^\circ = -0.3469\ V.,$$

and taking the normal hydrogen potential as zero[1] the normal potential of the copper electrode is -0.3469 V.

If, instead of using the data for 0.0005 M solutions, we make a similar calculation using the data at 0.005 M, taking the average values of Noyes and Stewart, and making the same assumptions as to proportionality of activity and concentration, we find $\mathbf{E}^\circ = -0.3445$ V. The difference between this value and that obtained from 0.0005 M solutions, amounting to 0.0024 V., might possibly be due to errors in the freezing-point data which we have employed, but probably indicates that even at a dilution of 0.005 M the simple laws of dilute solutions do not hold accurately when bivalent ions are involved. We shall therefore accept as the best obtainable value for the *normal electrode potential of copper against cupric ion at 25°,* $\mathbf{E}^\circ = -0.3469$ *V.*, which is probably correct to about one millivolt.

A more obvious method of determining the normal electrode potential of copper is at present less accurate, but we have attempted to use this method also. Cells were constructed of the type: Cu, $CuSO_4$ 0.005 M, $CuSO_4$ 0.05 M, $MgSO_4$ 0.05 M, KCl 0.1 M, KCl 1.0 M, HgCl, Hg, giving $\mathbf{E} = +0.0232$ V. The first liquid potential $CuSO_4$ 0.005 M, $CuSO_4$ 0.05 M was calculated from the formula

$$\mathbf{E} = \frac{u - v}{u + v} \frac{RT}{2\mathbf{F}} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2}.$$

Taking u as 78.8 and v as 54.2, $\mathbf{E} = +0.0044$ V. This value must, however, be considered uncertain, as it is doubtful how valid the formula is in a case of this kind. The potential $CuSO_4$ 0.05 M, $MgSO_4$ 0.05 M may be neglected, since the mobilities of Mg^{++} and Cu^{++} are almost identical; in fact, the omission of $MgSO_4$ from the chain altered the total E. M. F. by only 0.0001 V. The potential $MgSO_4$ 0.05 M, KCl 0.1 M has been measured directly by Faragher[1] and found to be +0.0016 V. The potential KCl 0.01 M, KCl 1.0 M is calculated to be +0.0004 V. We have therefore exclusive of liquid potentials Cu, $CuSO_4$ 0.005 M || N. E.; E = 0.0168 V. Assuming that the concentration of Cu^{++} is 0.00315 M in $CuSO_4$ 0.005 M, and that the activity is proportional to the concentration, we calculate for the normal potential of copper against the normal electrode

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[1] Lewis, THIS JOURNAL, 35, 24 (1913). It should be emphasized that the potential so stated is not the same, either in magnitude or sign, as the value ϵ_h stated according to the recommendations of the committee of the Bunsen Gesellschaft.

$$\text{Cu, Cu}^{++} \,||\, \text{N. E.; } E^\circ = -0.0571 \text{ V.}$$

Now we have

$$\text{H}_2\text{, H}^+ \,||\, \text{N. E.; } E^\circ = +0.2776 \text{ V.}^2$$

and subtracting gives

$$\text{Cu, Cu}^{++} \,||\, \text{H}^+\text{, H}_2\text{; } E^\circ = -0.3347 \text{ V.}$$

which is the value obtained in this way for the normal potential of copper. This differs from the more accurate value obtained above by more than one centivolt. The large discrepancy is doubtless partly due to the assumption that the concentration and activity of Cu^{++} in $CuSO_4$ 0.005 M can be calculated directly from the conductivity, but is probably chiefly to be ascribed to the uncertainty in the liquid potentials, especially that between $CuSO_4$ 0.005 M and 0.05 M.

BERKELEY, CAL.

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THE TRANSFERENCE NUMBER, CONDUCTANCE, AND IONIZATION OF HYDRIODIC ACID AT 25°.

BY E K STRACHAN AND VEE GIH CHU

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1. Purpose of the Investigation. 2. The Transference Experiments. 3. The Relative Viscosities of Hydriodic Acid Solutions. 4 Conductance and Ionization. 5. Summary.

1. Purpose of the Investigation.

When the degree of dissociation of an electrolyte is calculated from the conductivity ratio in the usual manner, the assumption is made that the relative mobilities of the ions and hence also the transference numbers for the electrolyte are independent of the concentration. This assumption is approximately true for most dilute salt solutions, but in some instances, notably in the case of lithium chloride,[1] the condition is apparently not fulfilled. In the case of strong acids, also, the transference number in the concentration range 0.005 to 0.1 normal, as obtained by direct measurement, is not in agreement with the ordinarily accepted value for the conductance of the hydrogen ion at infinite dilution.[2]

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[1] This work is about to be published.

[2] Based upon measurements of Sebastian about to be published.

In such cases the degree of ionization may be calculated from the values of the *individual ion conductances*, as explained in a previous paper.[3] The expression, there derived, for the degree of ionization, γ, of hydriodic acid is

$$\gamma = \frac{\Lambda T_I}{\Lambda_{0I}}\left(\frac{\eta}{\eta_0}\right) \qquad (1)$$

in which Λ is the equivalent conductance of the hydriodic acid solution, (η/η_0) is its relative viscosity, T_I is the transference number of the iodide ion constituent in the solution and Λ_{0I} is the equivalent conductance of the iodide ion at infinite dilution.

At the time of the investigation referred to, the above data were not available in the case of hydriodic acid solutions. Consequently the conductances of several such solutions were determined and these values, together with some preliminary values of the transference number, were made the basis of the calculations in the previous paper. Since then other more careful and complete conductance determinations have been made and the transference measurements completed. It is the purpose of the present paper to present the results of these determinations and the values of γ to which they lead.

2. The Transference Experiments.

The transference number was determined by the Hittorf method, using a silver anode and a silver iodide cathode. At the end of each experiment three middle portions as well as both electrode portions were analyzed in order to make sure that no mixing had occurred.

The apparatus employed is shown in the accompanying diagram (Fig. 1). In order to prevent mixing from convection currents due to local heating, the constricted portions of the apparatus were, with one exception, placed at the top so that the heated portions could not rise and cause stirring. The exception occurs in the stopcock at the bottom of the anode section, *A*. This was made small on account of the difficulty in constructing one with a bore as large as that of the rest of the apparatus. Convection currents at this point, however, could cause stirring only within the anode portion and so would result in no harm. The apparatus was made in three sections, which were connected by rubber tubing at the points

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[1] Cf. Washburn, *Proc. Amer. Electrochem. Soc.*, **21**, 134 (1912).

[2] See Noyes and Falk, THIS JOURNAL, **33**, 1460 (1911).

[3] Washburn and Strachan, THIS JOURNAL, **35**, 690 (1913). See, further, Washburn, *Loc. cit.*

d and *e*. The anode portion extended from the anode, *A*, to the stopcock, and the cathode portion from the cathode, *C*, to the dotted line *c*. The remainder of the apparatus was designed to contain the three middle portions which are called the anode middle, the middle, and the cathode middle, and are designated, respectively, by the letters M_a, M, and M_c.

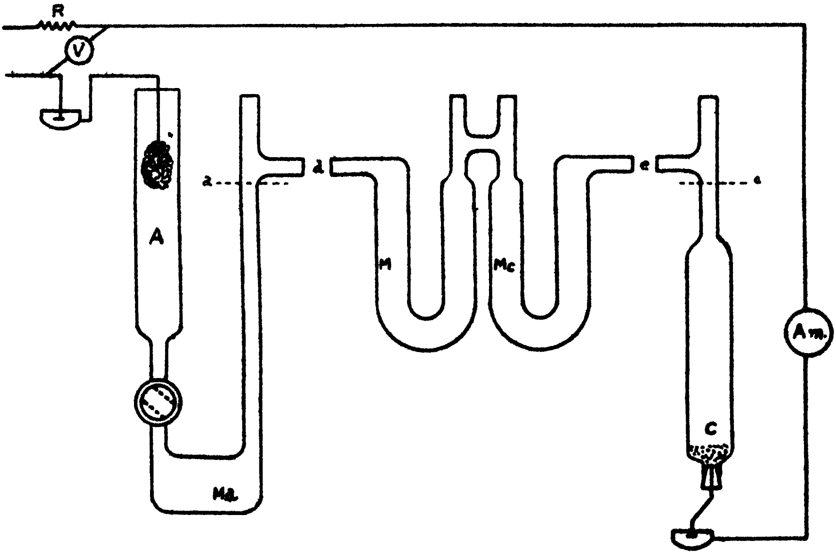

Fig. 1.

The three sections of the apparatus were of such sizes that the portions of the solution withdrawn for analysis amounted to about 250 cc. each, thus making it possible to secure an accuracy of about 0.01% in the analyses of the more dilute solutions.

The anode consisted of a silver spiral made of several hundred turns of fine wire in order to obtain a large electrode surface. Before using, it was cleaned by dipping in warm nitric acid until it was violently attacked, and then washing several times with water. After being dried, it was suspended in the top of the anode section of the apparatus and connected as shown in the figure. The cathode consisted of a few turns of silver wire which had been cleaned in warm nitric acid and coated with a thin layer of silver iodide by electrolysis. The wire so prepared, after it had been placed in the transference apparatus, was covered with an excess of freshly precipitated silver iodide as indicated in the figure.

The silver coulometers used in this investigation were of the ordinary filter paper type, the cathode consisting of a platinum dish and the anode of a silver button wrapped in filter paper. One coulometer was connected to the anode, and the other to the cathode as shown in Fig. 1, in order to detect any loss of the current that might occur during the experiment.

Preparation of Materials. Water.—All water used was conductivity water obtained from a special still.

Hydriodic Acid.—Iodine was distilled from potassium iodide solution, and then reduced by yellow phosphorus and water. The resulting crude product was distilled twice in an atmosphere of hydrogen, and yielded a perfectly colorless distillate which boiled at 127°. Solutions of various concentrations were prepared by diluting this acid with the requisite amount of air-free distilled water, the exact concentration being determined by precipitating the iodine as silver iodide. In some of the earlier experiments the crude acid was distilled in contact with the air. The distillate in those cases was colored dark brown by the free iodine. When this had been removed by shaking the solution with benzene, the same transference number was obtained as when the originally iodine-free acid was used. These earlier experiments are, therefore, included with the later. During the transference experiments some free iodine appeared in the solution, owing to the reaction $4HI + O_2 = 2H_2O + 2I_2$, but this was shown by analysis never to exceed a few hundredths of a per cent.

The *silver nitrate* used both for the analyses and in the coulometers was Kahlbaum's c. p. salt. A 20% solution was used in the coulometers. It was usually freshly prepared, and never used more than twice. A 0.03 normal solution was used in the analyses.

Experimental Procedure.—The apparatus was thoroughly cleaned and dried, and the three glass parts placed in the supports and joined at *d* and *c*. The electrodes were inserted and the cathode covered with about 3 g. of freshly precipitated silver iodide which had been washed repeatedly with the solution to be used in the experiment. Then the cathode side was filled with the solution, care being taken not to stir up the silver iodide on the electrode. To accomplish this the solution was poured very slowly through a dropping funnel with a long stem, at the lower end of which was an upward hook with a small opening. While the hydriodic acid was being added the funnel was gradually raised so that the liquid would be delivered just at the surface of the solution already in the apparatus. After this the other sections of the apparatus were also filled with the solution. Air bubbles were removed by means of a clean dry rod. The anode spiral was fixed so as to occupy a position about three centimeters above the stopcock. This left considerable solution above the electrode, which stirred slowly during the run and prevented the exhaustion of the electrolyte in the immediate vicinity of the electrode. To prevent any leakage of the solution or current, all joints of the apparatus were covered with liberal amounts of melted beeswax, and the lead wire from the cathode was conducted out of the bath through a rubber tube. The whole apparatus was then placed in the thermostat to such a depth that the water of the bath and the solution in the apparatus were at the same level so as to eliminate hydrostatic pressure. The electrical connections were then made as shown in the diagram.

After the solution had come to the temperature of the thermostat, which was maintained at 25°, the circuit was closed, and the rheostat, *R*, adjusted to give the proper current strength. The strength of the current and the duration of the experiment varied with the concentration of the solution. In most cases the current was about 30 milliamperes, and the time about eight hours.

As soon as the experiment was completed, the circuit was broken and the stopcock closed. Then by introducing a clean, dry pipet into the apparatus through the small tubes at the top, samples of the three middle portions were obtained. These were transferred to tared Erlenmeyer flasks and weighed. After the removal of these portions the anode and cathode lead wires were disconnected, the apparatus taken out of the thermostat and dried on the outside. It was then disconnected at *d* and *c* and the anode and cathode sections were stopped with paraffined rubber stoppers. Next, the glass stopcock in the anode section was opened and the anode portion mixed thoroughly by shaking. The contents of the cathode section were mixed in a similar manner. The two parts of the apparatus containing the electrode portions were then cleaned and dried on the outside and weighed to the nearest milligram. As much of the clear solution from the anode as possible was then transferred to a tared Erlenmeyer flask, weighed and analyzed. The anode section, together with the silver spiral, was washed, dried with alcohol, and weighed. This weight, subtracted from the weight of the anode section filled with the solution, gave the weight of the anode portion. The bulk of the cathode portion was filtered through a tared Gooch crucible into a clean, dry filter flask. The filtrate was immediately transferred to a tared Erlenmeyer flask and weighed, and served as the sample for analysis. The residue from the cathode, which consisted of gray metallic silver and silver iodide, was left in the Gooch crucible, and was washed, dried and weighed. The empty cathode section was also cleaned, dried and weighed. In order to obtain the weight of the total cathode portion the weight of the cathode section plus the weight of the silver and iodide in the Gooch crucible was subtracted from the weight of the cathode section before it was emptied.

All the solutions were analyzed by precipitating the iodide as silver iodide by a 0.03 normal silver nitrate solution. Before precipitation, the hydriodic acid solution was decolorized with a few drops of sodium sulfite and then diluted to 0.03 normal. Baxter[1] has shown that at this concentration of hydriodic acid and silver nitrate there is little danger of occlusion taking place during the precipitation.

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[1] *Proc. Am. Acad. Arts and Sci.*, 41, 78 (1905).

Calculation of Results.—The calculation of the transference numbers given in Table I was made in the following manner. The mass of water in the electrode portion was obtained by subtracting from the weight of the portion the weight of hydriodic acid contained in it. The mass of the water was then multiplied by the ratio of hydriodic acid to water in the original solution, and thus the mass of hydriodic acid in that amount of water before electrolysis was obtained. To determine the mass of hydriodic acid transferred, the mass of hydriodic acid present in the electrode portion before electrolysis was subtracted from that present after electrolysis in the case of the cathode portion, and *vice versa* in the case of the anode portion. The transference number of the cation was obtained by dividing the number of equivalents of hydriodic acid transferred by the number of equivalents of electricity passed through the solution.

The results of the transference-number measurements are given in Table I, the number at the top of each column being the number of the experiment. Concentrations are expressed in equivalents per 1000 g. of solution.

TABLE I.—TRANSFERENCE NUMBER OF HYDRIODIC ACID AT 25° DATA AND RESULTS.

	1.	2.	3.	4.
Concentration	0.2	0.16	0.09	0.06
Wt. Ag in coulometer A	1.3272	1.0084	0.6891	0.7239
Wt. Ag in coulometer C	1.3269	1.0076	0.6886	0.7239
Wt. electrode portion A	197.313	203.471	192.58	202.811
Wt. electrode portion C	237.704	239.261	236.663	236.376
% HI in portion M_c	......	2.1064	1.1897	0.70501
% HI in portion M	2.6527	2.1060	1.1889	0.70452
% HI in portion M_a	2.6528	2.1070	1.1888	0.70392
% HI in portion A	2.0112	1.6317	0.84169	0.36619
% HI in portion C	3.1818	2.5085	1.4686	1.0233
Equivalents of electricity	0.012301	0.009344	0.0063859	0.006710
Grams HI transferred (A)	1.2987	0.9859	0.6762	0.7076
Grams HI transferred (C)	1.2915	0.9839	0.6700	0.7035
Transference no. of cation (A)	0.825	0.825	0.828	0.825
Transference no. of cation (C)	0.821	0.823	0.820	0.819

The values of the transference number contained in Table I are summarized in Table II.

TABLE II.—TRANSFERENCE NUMBER OF HYDRIODIC ACID AT 25°.

	Transference number as calculated from	
Concentration.	Anode portion.	Cathode portion.
0.20	0.825	0.821
0.16	0.825	0.823
0.09	0.828	0.820
0.06	0.825	0.819
Mean	0.826	0.821
A. D.	0.001	0.001

An examination of the table shows that the value of the transference number calculated from the cathode portion is in every case smaller than that calculated from the anode portion. This difference is greater than the experimental error and requires an explanation. It can not be attributed to the formation of the slow moving AgI_2^- ion at the cathode, for a simple calculation shows that this ion could move toward the anode but a few centimeters during the course of the experiment, and so could not remove any iodine from the cathode portion.[1] The source of the discrepancy in the values obtained from the two electrode portions undoubtedly lies in the adsorption of some of the acid by the silver iodide cathode. The concentration of acid in contact with the cathode may change during the course of the experiment from about 0.1 normal to 0.4 normal or higher. It is to be expected that the silver iodide will adsorb a greater amount of acid in contact with the stronger solution. Any acid so adsorbed would be removed when the silver iodide was separated from the cathode portion of the solution. Consequently the value of the transference number derived from the cathode portion would be too small. A brief experiment was made in order to test this hypothesis. A weighed amount of silver iodide was shaken with a weighed amount of hydriodic acid solution, the strength of which was accurately known. After having stood over night a portion of the acid was removed and analyzed. In this way it was found that, after correction was made for the water originally present in the silver iodide, 5 g. of the latter had removed 0.0190 g. of acid from a 0.1 normal solution, and 0.0256 g. from a 0.4 normal solution. This result is not in quantitative agreement with the results of the transference experiments, yet is sufficiently close to show the cause of the discrepancy, and to indicate this as the probable source of error in the above transference experiments. For this reason the value 0.826 obtained from the concentration change of the anode portion has been adopted as the transference number of the cation of hydriodic acid.[2] Within the concentration range studied it appears to be independent of the concentration.

3. The Relative Viscosities of Hydriodic Acid Solutions.

We are indebted to G. Y. Williams for measurements of the viscosity of the acid in the quartz viscosimeter devised in this laboratory.[3] Two solutions were examined, one of 0.1963 normal concentration, and the other 0.09839 normal, and their relative viscosities found to be 0.99542 and 0.99660, respectively. Values of the viscosity at other concentrations were obtained by linear interpolation.

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[1] That some $HAgI_2$ is formed at the cathode is evidenced by the slight precipitate of silver iodide which occurred when the cathode portion was diluted preparatory to analysis. Such a precipitate occurred only when the stronger solutions of acid were used, and then, of course, was filtered out of the solution before proceeding with the analysis.

[2] An additional reason for accepting this value as the correct one is the fact that when it is substituted in the equation $\Lambda_H = \Lambda/Ta - \Lambda_0 1(\eta_0/\eta)$ the value 364 is obtained for the equivalent conductance of the hydrogen ion, which agrees with the observations of Noyes and Sammet based on transference experiments with hydrochloric acid, *loc. cit.* For values of Λ and (η_0/η) see Table III.

[3] Washburn and Williams, THIS JOURNAL, **35**, 737 (1913).

4. Conductance and Ionization.

The conductance measurements were made by the Kohlrausch method, the pipet form of conductance cell in use in this laboratory,[1] and the extended bridge wire described by Washburn and Bell[2] being employed. All of the glass apparatus employed in handling the solutions was cleaned with warm chromic acid cleaning-mixture and steamed out for several hours before being used. The conductivity water was obtained from a special still and had a specific conductance of 0.6×10^{-6} mhos at 25°. Two stock solutions of hydriodic acid were prepared, one being about 0.2 normal and the other about 0.02 normal. Each was carefully analyzed by precipitating the iodide as silver iodide. The rest of the solutions were made by diluting weighed amounts of the stock solutions with weighed amounts of conductivity water.

Immediately after the preparation of each solution its conductivity was measured. The solutions remained almost if not quite colorless during the determination. After filling the conductance cell, it was placed in the thermostat at 25 ± 0.01°, and left there a short time. The conductance was then measured twice at intervals of fifteen minutes, in order to be sure that the solution had attained the temperature of the bath. The cell was then emptied and refilled with the solution and another measurement made. The various determinations of the conductance of the same solution agreed within less than 0.02%. The conductance cell was one that has been in use in this laboratory for a number of years, and has a cell constant of 0.6222. It was calibrated again by means of a 0.1 normal solution of potassium chloride just before being used in this investigation, and the constant found to be unchanged.

The results of the conductance measurements are shown in Table III. Column I contains the concentrations in equivalents per liter of the various solutions measured, and Column II their respective equivalent conductances expressed in reciprocal ohms. Column III contains the densities corresponding to the concentrations shown in Column I. The figures in Column V are the equivalent conductances at the round concentrations shown in Column IV. They were obtained from the figures in Columns I and II by graphical interpolation. The conductances of solutions above 0.01 normal were read off a curve obtained by plotting the equivalent conductance, Λ, against the concentration, C. In order to arrive at the conductances at round concentrations below 0.01 normal and the conductance at zero concentration, $1/\Lambda$ was plotted against

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[1] Washburn and MacInnes, This Journal, 33, 1686.

[2] Washburn and Bell, *Ibid.*, 35, 177.

$(C\Lambda)^n$ in the usual way, employing different values of n until one was found that made the curve nearest to a straight line. In this way 0.40 was obtained as the value of n. The equivalent conductance at zero concentration was found to be 426.2. The equivalent conductance of the iodide ion may be taken to be 76.5, which makes that of the hydrogen ion appear practically 350, a result obtained by a number of observers. The measured values of Λ for the concentrations 0.002 and 0.001 normal fall below the curve drawn through the points corresponding to the values shown in Column of V the table. Owing to the uncertainty which exists as to what water correction should be applied to the measured conductances of very dilute solutions, it is difficult to state whether the interpolated or the measured values are the most nearly correct. Other observers have noted the same phenomenon.[1] The water correction was applied by subtracting the specific conductance of the water from that of the solution.

TABLE III.[2]—CONDUCTANCE AND DISSOCIATION OF HYDRIODIC ACID AT 25°. 1913 ATOMIC WEIGHTS.

I. C.	II. Λ.	III. D_4^{25}	IV. C.	V Λ.	VI. η/η_0.	VII. $\gamma = \Lambda Ta/\Lambda_{0}1(\eta/\eta_0)$	VIII $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)$
0.2217	381.2	1.0181	0.200	383.0	0.9954	86.71	89.45
0.1124	391.8	1.0082	0.100	393.6	0.9966	89.21	92.04
0.05435	400.4	1.0025	0.050	401.2	0.9980	91.07	93.95
0.02507	406.6	0.9996	0.020	408.2	0.9992	92.77	95.70
0.01036	412.2	0.9980	0.010	412.4	1.0000	93.80	96.76
0.005144	415.5	0.9975	0.005	415.7	1.0000	94.55	97.54
0.002152	417.5	0.9972	0.002	418.7	1.0000	95.23	98.24
0.001009	418.6	0.9971	0.001	420.5	1.0000	...	98.66
....	...	0.9971	0.000	426.2	1.0000	...	100.00

In Column VII of the table, values of the degree of dissociation of the acid calculated by use of the formula $\gamma = \Lambda T_{I}/\Lambda_{0I}(\eta/\eta_0)$ are given, and in Column VIII, for the sake of comparison, values calculated by use of the relation $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)$. The difference in the two sets of values is about 3%.

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[1] Goodwin and Haskell, *Proc. Am. Acad.*, 40, 514; Bray and Hunt, THIS JOURNAL, 33, 786 (1911).

[2] The values of the degree of dissociation shown here differ from those used in calculating the equilibrium between arsenious acid and iodine (THIS JOURNAL, 35, 690) by about 1%, the discrepancy being due to an error in calculating the concentrations of the solutions employed in the former investigation. The figures shown here indicate that the true value of the arsenious acid iodine equilibrium is 4% higher than that given (*loc. cit.*), that is, 5.76×10^{-2} in place of 5.54×10^{-2}, a difference, however, which is within the experimental error in determining this constant. Another more serious error occurs in Part III of the former investigation where the details of the calculation of the heat of the reaction are presented. Some of the thermochemical data employed in this calculation were not corrected for the work of the process. When these corrections are made a heat effect of 1540 calories is obtained and this heat effect indicates that the equilibrium constant *decreases* with rise in temperature, a result which is contrary (in sign) to the observations of Roebuck. This result is probably to be attributed to errors in some of the thermochemical data employed, and the question of the value of the heat of the reaction must be left open until the equilibrium has been studied at another temperature.

Since no transference numbers have been determined at concentrations lower than 0.002 normal, corresponding values of the degree of dissociation are not shown in Column VII. In fact no measurements of the transference number of hydriodic acid have been made at concentrations less than 0.05 normal. However, since neither the transference number of hydrochloric[1] nor that of nitric acid[2] shows any marked change of value in the range 0.05 to 0.002 normal, it is probable that that of hydriodic acid also does not. Consequently the ionization values are shown at concentrations as low as 0.002 normal. The formula presented in the introduction, if applied to the figures shown in Table III using the transference number 0.174, would indicate only 97% dissociation at infinite dilution. As has been pointed out, either the transference number is different at these low concentrations, or what seems much more reasonable, the conductance measurements are at fault.

5. Summary.

1. The transference number of the cation of hydriodic acid at 25° is 0.826 ± 0.001 between the concentrations 0.2 and 0.06 normal.

2. The conductances of hydriodic acid solutions have been measured and the degree of dissociation calculated for the concentration range 0.2 to 0.002 normal.

3. Adsorption of hydriodic acid by silver iodide is shown to be a source of error in transference experiments made with a silver iodide cathode.

We desire to express our indebtedness to E. W. Washburn for his kind criticism of this work.

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THE PURITY OF FUSED LITHIUM PERCHLORATE, AND ITS BEARING UPON THE ATOMIC WEIGHT OF SILVER.[3]

BY THEODORE W. RICHARDS AND MARSHALL W COX

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In a comprehensive research upon the atomic weights of lithium and silver, H. H. Willard and one of the present authors[4] devised and perfected an entirely new method for determining the latter of the two atomic weights. This method involved the treatment of pure anhydrous lithium chloride with excess of perchloric acid, and the drying of the lithium perchlorate thus formed for a long time in a state of fusion at a temperature of about 300°. From the weights of factor and product, together with the ratio of lithium chloride to silver (determined at the same time in another series of analyses made in the usual way), it is easy to calculate the atomic weight of silver with reference to that of oxygen in the following fashion. Assuming that four times the atomic weight of oxygen is 64.000:

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[1] Noyes and Sammet, THIS JOURNAL, **24**, 944 (1902); **25**, 165 (1903).

[2] Noyes and Kato, *Ibid.*, **30**, 318 (1908).

[3] A brief notice upon this topic was presented to the Eighth International Congress of Applied Chemistry in New York in September, 1912, and printed in the *Original Communications of this Congress*, **25**, 157.

[4] Richards and Willard, *Publ. Carnegie Inst.*, No. 125.

$$\frac{\mathrm{Ag}}{64.000} = \left(\frac{\mathrm{LiCl}}{\mathrm{LiClO_4} - \mathrm{LiCl}}\right)\frac{\mathrm{Ag}}{\mathrm{LiCl}}$$

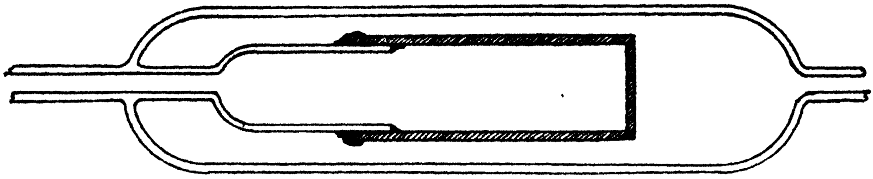
The value of the outcome depends as usual upon the purity of the three solid substances concerned. Silver is capable of being made nowadays in a state of great purity. Lithium chloride also can be prepared in a state very free from contamination, even with water, by methods elaborated at Harvard; but lithium perchlorate, which has been less studied, cannot be heated to a red heat without decomposition, and its freedom from volatile impurities is less certain. This fact was fully appreciated by the experimenters, and they promised to investigate further the question concerning the purity of the lithium perchlorate.

Obviously, any water retained by this salt would decrease the apparent atomic weight of silver, by increasing the denominator of the fraction within the parenthesis. On the other hand, any trace of decomposition suffered by the salt would have the opposite effect. The resulting contamination of the perchlorate by chloride or chlorate is easy to detect; but the retention of minute traces of water is much more difficult to discover. The present investigation, which has been greatly prolonged because of the subtle nature of the problem, has primarily to do with the question as to the anhydrous condition of the lithium perchlorate, and we take pleasure in stating that the question, if not wholly settled, has now at least been carried much further than before. The evidence now available points towards the improbability of the retention of weighable amounts of water by lithium perchlorate at 300°. It is true that this result was not wholly unexpected, for the salt came to satisfactory constancy in weight, even at 280°, and a rise of 30° had no effect upon this weight. Moreover, one of us, in collaboration with G. S. Forbes, showed, some time since, that silver nitrate, a salt nearly as soluble as lithium perchlorate, retained practically no water at all at a much lower temperature, namely, 200°. Nevertheless, the outcome is satisfactory, and leads one to believe that the method under discussion for determining the atomic weight of silver is one of the very best.

At first sight the problem involved in determining the trace of water possibly held by the salt might appear to be a simple one. It is merely necessary to decompose pure lithium perchlorate (which has been fused and dried to constant weight at 300°) and to determine the weight of water which may be evolved among the products of decomposition. But in decomposing a salt by heat under these conditions a portion of the solid is carried along with the stream of gas in a state of subdivision so fine as to evade capture in any ordinary train of purifying towers. If the complication of this train is greatly increased, the chance of losing a trace of water altogether on the one hand or fortuitously collecting water from some other source is a serious one.

Two methods of attack were considered. At first it was thought that oxygen and water, and any trace of chlorine evolved, might be condensed together by means of liquid air. The powder would then be held in the condensed liquid, and would doubtless be left behind when the oxygen was allowed to evaporate.[1] The problem of driving the water off from the remaining small amount of solid and collecting it in phosphorous pentoxide would obviously be easy.

After several trials, however, this method was abandoned in favor of another, yet simpler. The gas evolved by decomposing the perchlorate, carrying with it exceedingly fine powder and traces of chlorine, was passed first through a warm coil of closely packed finely divided silver wire to remove the chlorine, and then through a porous porcelain dry-filter or "dust-trap" to remove the powder. The water in the gas thus purified could be easily determined in the usual way.



Dust-trap.

The shaded portion indicates the porous cylinder; the black spots show where silver chloride was used as cement.

The coil of silver wire is an old device for the purpose of removing undesired chlorine. Its efficiency was shown by the fact that the portion of the silver nearest to the decomposing salt was tarnished, whereas the greater part of the coil kept its original lustre through many experiments.

The "dust-trap" also is not an entirely new idea. It was used by one of us in collaboration with Köthner and Tiede, in an investigation upon the atomic weight of nitrogen in 1907.[2] For the present purpose it was necessary to construct a filter which would certainly neither retain a trace of the water, nor evolve any into the stream of air passing through it. Moreover, the pores of the filter must be so fine as to allow no appreciable weight of the fine dust from the decomposing salt to pass through them. After a number of experiments we found that a fine-grained unglazed "Pukal" porcelain cup, of the sort used in the coulometer or voltameter in 1899,[1] and since so strongly recommended for the purpose by E. B. Rosa, answers admirably. As a cement to connect this porcelain to the rest of the apparatus, fused silver chloride was found to be the most convenient substance. Each question involved was of course carefully tested. In the first place, a cup (previously cleaned by washing thoroughly with nitric acid and soaking for several days in many portions of distilled water until all acid was removed), was dried in an electric oven, cooled in a desiccator and weighed. The cup was now moistened with water, and again dried at 300°, cooled and weighed. This was done three times, with the result that during the whole period the cup remained constant in weight within two-hundredths of a milligram, the limit of the sensibility of the excellent balance used.

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[1] This method was proposed by one of us in 1907, and was used with success in a somewhat analogous case by Stähler and F. Meyer, *Z. anorg. Chem.*, 71, 378.

[2] *Z. anorg. Chem.*, 61, 320 (1909); THIS JOURNAL, 31, 6 (1909). Others also have doubtless employed it.

In order to test the fineness and evenness of grain of the cup, and to be sure that it was properly cemented to its glass support, it was wholly submerged in water after it had been cemented into place, and air was forced through it under pressure. If small bubbles formed rather slowly over the whole surface of the porcelain, sufficient evidence was obtained that air really passed through the many small passages in the walls, but if a rush of bubbles appeared from one or two points, the cup was obviously imperfect and was discarded. A similar test might be applied with advantage to cups used for the coulometer. No great trouble was experienced in finding cups which would pass this test; the main difficulty usually appeared where the porcelain was cemented to the glass. Very pure silver chloride, free from any infusible impurities or dust, was required to serve as a cement if a perfect joint was to be made.

Obviously it was necessary to collect in a perfectly unaltered condition all the gas emerging from the "dust-trap." Accordingly the porcelain cup was surrounded with a slightly larger glass tube. This wide tube was sealed by an inside joint to the narrow tube bearing the cup, and the open end of the surrounding jacket was drawn down to a small tube which could be connected with the quantitative drying apparatus. The completed dust-trap is shown in Fig. 1; it would allow air to pass under moderate pressure at the rate of two or three ordinary bubbles per second, and maintained its efficiency through a long series of experiments.

The air-filter thus constituted was found to be so efficient in its operation and so free from any disturbing effect that another one of the same type was used in purifying the air used for drying the perchlorate before its decomposition. The fact has long been known that minute particles of

[1] Richards and Heimrod, *Proc. Am. Acad.*, 35, 123 (1899); *Z. physik. Chem.*, 32, 339 (1900).

dust not visible to the naked eye may be carried in a current of gas through many feet of tubing, or even, in bubbles, through deep layers of liquid. Clearly, then, it is important whenever a substance is to be dried in a considerable current of air, that this dust should be eliminated; for it might easily contaminate to some extent the pure substance to be treated. As will be shown, the outcome in the present case justified these considerations in a striking way, and indicated that in any such case a "dust-trap" of this sort should be employed if the highest accuracy is sought. This outcome in its bearing upon accurate work in general is one of the most interesting of the points enforced by the present research.

The point is most clearly demonstrated by a comparison of the experience of different experimenters upon lithium perchlorate. Potilitzin[1] found that the decomposition of lithium perchlorate into chlorate and chloride proceeded very rapidly at 268°. Richards and Willard were able on the other hand to subject the salt to continued treatment at 300° with a barely perceptible trace of decomposition. Their salt and the air with which it was in contact were both doubtless much purer than Potilitzin's; evidently impurities incite catalytic decomposition. At 350° the two Americans found that the salt decomposed so violently as to throw visible particles of dust through several feet of tubing; but in the present research lithium perchlorate dried and fused in a current of carefully filtered air, (otherwise precisely similar to that used in the research of 1910) could be heated for three or four hours at 400° with very slight decomposition and with no visible projection of material nor exit of gas. Only at 430° or a higher temperature did decomposition proceed with rapidity or completeness. Moreover, it was possible so to regulate the temperature between 410° and 430° that the decomposition was slow and the current of outgoing gas flowed quite steadily at the rate of from two to three bubbles per second. This previously unobserved stability of lithium perchlorate was doubtless due to the very high degree of purity of the material, probably never before attained; and the chief cause of this purity seems to have been the exclusion of impalpable and invisible dust from the current of many liters of air which passed over the salt during its synthesis, crystallization and long-continued drying in a fused condition. The exact mechanism of this catalytic effect cannot be studied quantitatively until the nature of this trace of dust is discovered; possibly the finely powdered steel, which is said to exist in the air of all cities, is responsible. Enough has been said to show that the air-filter served an important office, and to suggest that in other investigations also, where great purity is sought, its help should be employed.

The lithium perchlorate employed in the present work was prepared from very pure materials made several years ago by H. H. Willard and remaining from the research on atomic weights already mentioned. We are greatly indebted to him for this service. Lithium chloride free from any other base or acid was treated by slight excess of the purest aqueous redistilled perchloric acid in a flask of fused quartz as described in the earlier research.[1] The evaporation of the water and excess of acid into a current of dry or moist air at gradually rising temperature was also conducted as before. In this way samples of salt fused and dried at 300° were prepared in a condition duplicating closely the portion weighed by the previous investigators. The only difference already mentioned lay in the greater care taken to free the air-current from dust and other impurities. To this end, the air, drawn directly from out-of-doors by a water pump, was forced by the same pump over nearly fifty centimeters of hot copper oxide, through two towers containing potassium hydroxide solution containing a little manganate, through other towers containing a little potassium permanganate, over fused potassium hydroxide, through another shorter tube of red hot copper oxide, again over a large quantity of fused potassium hydroxide, over fifty centimeters of the best obtainable phosphoric pentoxide, that had previously been resublimed in an electrically heated apparatus, and finally through a dust-trap which was placed just before the flask in which the lithium perchlorate was synthesized. The object of the tube of hot copper oxide was to eliminate the trace of hydrogen or hydrocarbon which may exist in the air of cities; the objects of the other tubes are sufficiently evident without explanation. The air filter or dust-trap was placed at the end of the train so that any dust which might have been carried away from any part of the train itself might be eliminated.

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[1] See Abegg, "Handbuch der anorganische Chemie," quoting from Potilitzin, *J. Russ. Phys. Chem. Soc.*, 20, I, 541 (1888).

No rubber connections were used in this system; it was all fused together except when the juxtaposition of hard and soft glass necessitated ground joints.

Before attempting to measure any moisture that might be retained by the lithium perchlorate, it was necessary to prove that no weighable quantity of water passed through this elaborate drying train. The test was effected by means of a weighed U tube of phosphoric pentoxide as usual. Of course great care was bestowed on the preparation and handling of this tube, since faulty technique here would vitiate the whole work. The tube possessed two tightly fitting glass stopcocks; it had been scrupulously cleaned and was filled with very pure resublimed phosphoric pentoxide. After the work had once begun, this tube was never touched with the hands, but was handled by means of chemically clean cloths or by platinum-tipped forceps. The least possible lubricant of paraffin and fused rubber was used on the stopcocks, and a vanishingly thin layer of the same lined the rubber connectors by which the tube was connected with the train. After a test, only the side-arms of the tube were wiped with several thicknesses of a dry chemically clean cloth. Before each weighing, the U tube was allowed to remain over night under a bell-jar containing a small dish of sulfuric acid. An exactly similar tube, to be used as a counterpoise, containing glass pearls, was kept under a separate similar bell-jar. Before weighing, the tubes were allowed to adjust themselves to the conditions obtaining in the balance case, the air pressure and in both the tube and its counterpoise was made equal to that in the room by very brief opening. An excellent balance, previously used in many atomic weight determinations, was employed, and a tube containing radium bromide was kept in the case, to eliminate electric charges. Weighing took place by the method of substitution, the two tubes being placed on the balance alternately until perfect equilibrium was obtained. Under such conditions, successive weighings of the tube never but once differed from each other by more than 0.00002 g., and the single exception was 0.00003.g. This means that it was possible to weigh the minute quantity of water contained in two or three cubic centimeters of ordinary atmospheric air.

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[1] Richards and Willard, *Publ. Carnegie Inst.*, No. 125, pp. 39, 40 (1910).

After the long drying train had been swept out with pure air for a number of days, the tube of pentoxide was attached directly to the end of the drying train, in the position usually occupied by the quartz flask of lithium perchlorate, and air was passed through the whole for sixteen hours. During this time the tube gained but 0.00017 g. in weight. Without allowing the current of air to cease flowing, the empty quartz evaporating flask was placed in position and swept out for eight hours, and the pentoxide tube was attached to the side arm of this flask, while air continued to pass through for sixteen hours more. During this test, the tube showed a gain in weight of but 0.00020 g.—essentially the same amount as before. This quantity appeared to be a constant; two attempts to eliminate even this last trace of water by a condensing coil, submerged in liquid air, were unsuccessful.

The final control experiments were now obtained by placing the tube of silver wire and the second dust-trap in position beyond the quartz flask and passing air through the empty apparatus while the weighed tube of pentoxide was adjusted in its place beyond the dust-trap. Many experiments were made in this way, but in no case could a perfect control experiment be obtained. It is probable that moisture gains access during the fitting up of the apparatus, and the amount seemed to be not very different in protracted experiments from what it was during very brief ones. The gain in weight of the pentoxide tube varied from 0.0002 to somewhat over 0.0003 g. Two final control experiments made, one just at the beginning, of the series in which lithium perchlorate was decomposed, and one in the middle of that series, were conducted precisely under the conditions maintained in that series, except that in the control experiments no lithium perchlorate was present. In the first of the blank tests the tube of pentoxide gained 0.00028 g. during five hours; in the second, 0.00034 g., the average being 0.00031 g. Although it would have been more satisfactory to find the source of the water, this was not essential for our purpose, since constancy was all that was needed. As time pressed, and it was necessary to hasten the experiments, the decomposition of lithium perchlorate in this complicated apparatus was now undertaken. Five experiments were made; in three of these only a small amount of the salt was decomposed, although it was kept above 385° for over two hours; whereas in the other two experiments more than half of the lithium perchlorate was decomposed. In the first group the procedure was as follows: Very pure lithium perchlorate, prepared in the quartz flask by the evaporation of lithium chloride with a slight excess of perchloride acid, was heated in a current of dry air for at least five hours at a temperature of 280–300°. This gave samples of the salt in the same condition as the final weighed product of the previous investigators. At this stage the new pieces of apparatus, *i. e.*, the tube of silver wire and the dust-trap, were placed in position; and these were swept out over night by the same air that was passing over the lithium perchlorate, which was kept at 200° throughout that time. In the morning, while the current of air continued without interruption, the tube of silver wire was warmed until the hard glass barely showed a sodium flame, and the dust-trap was heated at 150°. At noon, the tube of phosphoric pentoxide, just previously weighed, was securely wired into position, and a protecting tube of pentoxide was added, so as to prevent any moisture from diffusing backwards into the weighed tube. The temperature of the perchlorate was then raised, during an hour, to the maximum used, and was held within 5° of that point during two hours. Finally the material was gradually cooled to 300°, at which point the pentoxide tube was removed to be weighed the next day. After further cooling, the lithium perchlorate was removed for weighing, so that the extent of its decomposition might be calculated. During the whole experiment, the air pressure in the apparatus was in the outward direction as shown by a mercury manometer sealed into the apparatus at a point just before the air entered the flask of perchlorate. Hence there was very slight opportunity for moist air to penetrate inwards. A new sample of lithium perchlorate was prepared for each experiment, amounting to from 10–15 g. The maximum temperature was 385° in the first experiment, 400° in the second, 400° in the third. The percentage of decomposition, assuming that all of the decomposed material was converted into chloride, varied from 0.033 % in the first to 1.25 % in the third experiment. The weight of water caught was in each case slightly less than that found in the control experiments, namely, 0.00020, 0.00027 and 0.00029 g. Hence no perceptible amount of water was evolved by raising the temperature of the fused perchlorate from 300° to 400°.

In the last two experiments the same procedure as before was followed, except that the perchlorate was heated to a higher temperature, which caused much more far-reaching decomposition. In the fourth experiment, the temperature of 450° was reached after one and one-half hours. At this point the evolution of oxygen was too violent and the experiment had to be stopped. Nevertheless, one would be inclined to think that if any water had existed in the salt it would have been expelled during these ninety minutes; but the tube of pentoxide showed a gain of only 0.00026 g. or less than that during the control experiments (0.00031).

A fifth experiment was more carefully regulated at between 410° and 430° during two hours, so that all the escaping gas passed through the weighed tube of pentoxide at a rate never exceeding three bubbles per second. The perchlorate (of which about three-quarters were decomposed) evolved bubbles and fine dust continuously, carpeting the whole apparatus as far as the dust trap with a thick film; but none could be seen beyond the porcelain cup in the trap. The pentoxide tube gained in weight by 0.00039 g., a trifle more than that shown by the two control experiments, (0.00031). It is possible that a trace of the powder, of almost molecular fineness, may have escaped the trap and caused this slight and unimportant difference.

In conclusion, the results show quite clearly that, within the limit of experimental error, no significant quantity of water can be expelled from lithium perchlorate which has been fused to constant weight, even when the temperature is raised to 430°, and most of the salt is decomposed. The first three experiments show an average gain in weight by the tube of pentoxide less than in the control experiments by 0.00006 g., while the two remaining experiments show an average gain greater than that of the average of the control experiments by but 0.00002 g. None of these differences is greater than the probable error of experiment, and even the largest is not large enough to have an important effect in the atomic weight of silver as found by the method of Richards and Willard. A tenth of a milligram of water in 15 g. of lithium perchlorate would lower the apparent atomic weight of silver calculated with the help of this salt by only about 0.001. Our results therefore seem to afford important evidence in confirmation of the value Ag = 107.871, found by those investigators.

A possible source of uncertainty in the interpretation remains to be considered. It is conceivable that a very small amount of water might be retained by lithium perchlorate without dislodgement up to the point of incipient decomposition, and beyond that point held in new combination as lithium hydroxide. Further consideration suggests arguments against this objection, however. We have found that the raising of the temperature by 130° (that is from 280° to 410°), a change amounting to about one-fifth of the original absolute temperature, causes no water to be evolved. One would expect that were water present in large enough quantity to be of importance, at least a fraction of it large enough to be detected, would have been volatilized before the salt suffered any decomposition at the higher temperature. Again, if any lithium hydroxide had been formed, might it not have attacked the flask, and thus have had its water set free, according to the equation $2LiOH + SiO_2 = Li_2SiO_3 + H_2O$? Usually the susceptibility of the containing vessels to attack is to be regretted, but here it would seem to be possibly more helpful than not.

Although the present paper cannot be considered as more than a preliminary attack upon the problem concerned, it serves to outline the difficulties and especially emphasizes them. With the added knowledge of lithium perchlorate now available, especially in regard to the greater stability of the salt when prepared in a dust-free condition, it will doubtless be possible to obtain an even more accurate evaluation of the ratio of oxygen to lithium chloride and hence of the atomic weight of silver than that found in 1910. It is hoped that this work may soon be undertaken in the Wolcott Gibbs Memorial Laboratory. We take pleasure in expressing our indebtedness to the Carnegie Institution of Washington for generous financial support.

Summary.

1. An effective air-filter or dust-trap for removing impalpable powder from a moderate current of air is described. The importance of its frequent use is emphasized.

2. Lithium perchlorate, prepared entirely in contact with air filtered through this contrivance, was found to be much less easily decomposed by heat than less carefully treated material.

3. The purest lithium perchlorate was found to decompose slowly at from 410° to 430° and rapidly at 450°.

4. It has been shown that no significant quantity of water can be driven out of fused lithium perchlorate by raising the temperature from 300° to 450°, even although most of the salt is decomposed at the higher temperature.

5. This outcome tends to confirm the use of lithium perchlorate as a basis for determining the ratio of oxygen to silver, and supports the value Ag = 107.871 found by Richards and Willard in 1910.

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COLORIMETRIC STUDIES ON THE NATURE OF CHROMATE SOLUTIONS.

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Received January 17, 1914

During the past quarter of a century many investigations have been made to determine the constitution and equilibria of chromates in aqueous solution. The preponderance of evidence previously and now contributed strengthens the conclusion that the most important equilibrium may be expressed by the equation:

$$H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4.$$

As will be shown in the following experiments, *the colors*[1] *of chromic acid, dichromates and chromates in solutions more dilute than 0.003% are identical,* that is, at these concentrations, both the chromic acid and the dichromates are completely[2] hydrolyzed, in accordance with the above equation. Furthermore, it will be shown that *heat*[3] *promotes the reversal of such reactions,* therefore, since the effect of hydroxyl and hydrogen ions has long been known, we have the following simple view of chromate solutions:

$$\left.\begin{array}{l}\text{Concentration}\\ \text{Heat}\\ \text{Acids}\end{array}\right\} (CrO_3)_n \rightleftharpoons H_2Cr_4O_{13} \rightleftharpoons$$

$$H_2Cr_3O_{10} \rightleftharpoons H_2Cr_2O_7 \rightleftharpoons H_2CrO_4 \left\{\begin{array}{l}\text{Dilution}\\ \text{Cold}\\ \text{Alkalies}\end{array}\right.$$

These reactions are assumed to involve only hydrolytic equilibria; however, when chromic oxide is dissolved in water and alkalies in varied proportions, many equilibria may be involved as typified by:

hydrolysis $\rightleftharpoons$ neutralization
hydration $\rightleftharpoons$ dehydration (condensation)
ionization $\rightleftharpoons$ association

Neutralization.

When chromic oxide is partially or fully neutralized with alkali, or is treated with an excess of the same (concentration and temperature remaining unchanged) the following reactions[4] are possible:

$$\text{I}\left\{\begin{array}{l}(a)\ 12CrO_3 + 3KOH \rightleftharpoons 3KHCr_4O_{13}\\ (b)\ 12CrO_3 + 6KOH \rightleftharpoons 3K_2Cr_4O_{13} + 3H_2O\end{array}\right.$$

[1] Ostwald (*Z. physik. Chem.*, **2**, 78) states that the colors of chromic acid and of chromates are identical. This is true only in the concentrations stated above Higher and equal concentrations of the two vary until the color of chromic acid is 2–3 times that of the dichromate.

[2] Moissan (*Compt. rend.*, **98**, 198; *Ann. chim. phys.*, [6] **5**, 568) doubted the existence of H_2CrO_4, so also did Field (*Chem. News*, **65**, 153) and others

[3] Hantzsch and Clark (*Z. anorg. Chem.*, **63**, 373) claim that light absorption of chromates is independent of heat, a conclusion which will be shown to be erroneous.

[4] Rammelsberg's hexachromate is very improbable. *Ann.*, **94**, 516.

$$\text{II}\left\{\begin{array}{l}(a)\ 12CrO_3 + 4KOH \rightleftarrows 4KHCr_3O_{10}\\(b)\ 12CrO_3 + 8KOH \rightleftarrows 4K_2Cr_3O_{10} + 4H_2O\end{array}\right.$$

$$\text{III}\left\{\begin{array}{l}(a)\ 12CrO_3 + 6KOH \rightleftarrows 6KHCr_2O_7\\(b)\ 12CrO_3 + 12KOH \rightleftarrows 6K_2Cr_2O_7 + 6H_2O\end{array}\right.$$

$$\text{IV}\left\{\begin{array}{l}(a)\ 12CrO_3 + 12KOH \rightleftarrows 12KHCrO_4\\(b)\ 12CrO_3 + 24KOH \rightleftarrows 12K_2CrO_4 + 12H_2O\end{array}\right.$$

Here it is observed that with 12 molecules of chromic oxide: (Ia) the minimum of alkali (3KOH) yields *acid tetrachromate*, which has not been isolated; (II*a*) an increase of alkali next yields *acid trichromate*, which also has not been isolated; (I*b*) and (III*a*) six molecules of alkali yield normal tetrachromate[1] and *acid dichromate*, the latter of which has not been isolated; (II*b*) eight molecules of alkali yield normal trichromate;[2] (III*b*) and (IV*a*) twelve molecules of alkali yield normal dichromate and *acid chromate*, the latter of which has not been isolated; (IV*b*) twenty-four or more molecules of alkali yield normal chromate. Since the acid chromates[3] have not been prepared, and since the tetrachromates and trichromates are unstable in the presence of water, investigations of chromates in aqueous solutions have been directed mostly to chromic acid, the dichromates and the chromates. Though most investigations show that alkalies,[4] dilutions and cold favor the formation of chromate, while acids, concentration and heat favor the formation of dichromate and chromic acid, intermediate products as (x), (y) and (z) may be involved, as indicated in the equation:

$$\left.\begin{array}{l}<H_2O\\<HO^-\\>A\end{array}\right\}\longrightarrow (CrO_3)_n \rightleftarrows x \rightleftarrows$$

$$H_2Cr_2O_7 \rightleftarrows y \rightleftarrows H_2CrO_4 \rightleftarrows z \longleftarrow \left\{\begin{array}{l}>H_2O\\>H^-\\<t\end{array}\right.$$

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[1] Siewert, *Z. ges. Naturw.*, **19**, 15; Schwartz, *Dingler's pol. J.*, **186**, 31; Wyruboff, *Bull. soc. chim.*, **35**, 162; Darmstädt, *Ber.*, **4**, 117; Jäger and Krüss, *Ber.*, **22**, 2037; Rammelsberg, *Ann.*, **94**, 516.

[2] See Siewert, Crookes, Jäger and Krüss, Bahr, *Jahresberichte*, **1853**, 358; Bothe, *J. prakt. Chem.*, **46**, 184; **60**, 60; Stanley, *Chem. News*, **54**, 194; Pries and Raymann, *Ber.*, **13**, 340; Wyruboff, *Bull. soc. ind. min.*, **1880**, 1882; Hauer, *Sitzb. Akad. Wiss Wien*, **39**, 439; Schroeder, *Ann.*, **174**, 249.

[3] The improbable formation of acid chromate was mentioned by Walden, *Z. physik. Chem.*, **2**, 73.

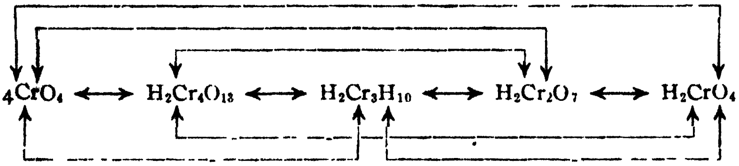
[4] Studies of the solubilities of products of the above reactions, involving sodium, potassium and ammonium kations, in different concentrations of the corresponding alkali, presents an interesting point of attack of the problem of chromate structures. For instance, chromic oxide is very soluble in water; ammonium and potassium dichromate are less soluble, while sodium dichromate is more soluble than the corresponding chromates; finally, the chromates are less soluble in the presence of an excess of alkali. Therefore, at least two maxima of solubility are indicated when chromic acid (12 mol CrO_3) is dissolved in increasing quantities (1–25 mols MOH) of alkalies. If other maxima are found, other molecules than $(CrO_3)_2$, $K_2Cr_2O_4$ and K_2CrO_4 will be indicated. Studies of this kind will be undertaken in this laboratory.

Hydrolysis.

Since, as will be shown below, chromic oxide can yield by hydrolysis chromic acid of the formula H_2CrO_4, we may assume the following successive hydrolytic changes:

$$4CrO_3 \longrightarrow H_2Cr_4O_{13} \longrightarrow H_2Cr_3O_{10} \longrightarrow H_2Cr_2O_7 \longrightarrow H_2Cr_2O_4$$

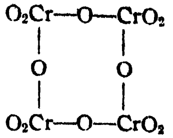
or as given in more detail·



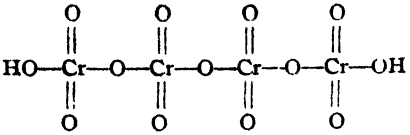
Since chromic acid and the alkali salts of the other four acids crystallize from solutions, it may be assumed that the molecules, constituting the masses separated, were assembled in solutions, hence existed, at least momentarily, in the solutions. The methods of preparation of chromic oxide and the polychromates, also the following colorimetric studies, corroborate this conclusion. Since all these reactions are reversible, aqueous solutions of chromic oxide may contain any or all of the above equilibria. Anhydrous solutions, as for instance, concentrated sulfuric acid, contain only chromic oxide; very dilute aqueous solutions (below 0.001%) contain only H_2CrO_4; intermediate concentrations contain the other three-- slightly acid solutions favor the formation of the dichromate, and successively increased acid solutions favor the higher poly-chromates.

The most probable assumption of the molecular complexity of chromic oxide is 4 CrO_3, for the following reasons: (1) four chromium atoms are found in tetrachromate, which is formed only in very concentrated solutions, while chromic oxide[1] is formed from anhydrous solutions; (2) alternate linking of four atoms of oxygen with four atoms of chromium, forming a ring, would not be unstable in accordance with Baeyer's strain-theory, whereas tri-, penta-, and higher molecular formulas would be unstable. If formula (*a*) is assumed for the oxide, it is easy to see how one molecule of water attaches itself so as to form (*b*) tetrachromic acid:

(*a*)



(*b*)



$$HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}{-}O{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}{-}O{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}{-}O{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}{-}OH$$

Also, it is easily seen how (*b*), by absorption of one, two, or three molecules of water, the lower chromic acids are formed:

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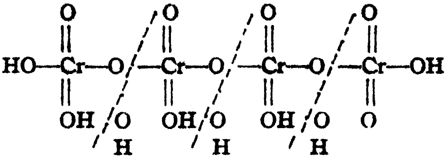
[1] Kremann, *Monatsh.*, 32, 619.

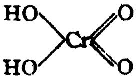


Here it is seen that tetrachromic acid—also chromic oxide—absorbs water and yields (1) four molecules of monochromic acid, (2) one molecule of dichromic acid and two molecules of monochromic acid, (3) one molecule of trichromic acid and one molecule of monochromic acid, or (4) two molecules of dichromic acid. The trichromic acid[1] yields (1) three molecules of monochromic acid, or (2) one molecule of dichromic acid and one molecule of monochromic acid. The dichromic acid yields two molecules of monochromic acid. Thus with the tetrachromic acid, four hydrolyses are possible; with the trichromic acid, two; with the dichromic acid, one. But since trichromic acid, dichromic acid and their hydrolytic products are identical with the products of tetrachromic acid, only four hydrolytic equilibria are indicated. If we add to these the initial hydrolytic action on chromic oxide, and the hydrolyses of the salts of all these acids, and furthermore, if we consider the hydration products of all the above molecules and their respective ionization-equilibria, it is seen that complicated systems of equilibria are involved in solutions of chromates, in the presence of acids and alkalies, in different concentration and under the influence of heat, light, etc. Some of these are indicated in the table on the following page.

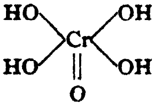
Hydration.

The following hydration-forms of monochromic acid may exist:

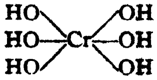
(a)



(b)



(c)



Dilution, cold and increase of alkali favor *a* ⟶ *c*; concentration, heat and decrease of alkali, *a* ⟵ *c*. These assumptions of hydration are supported by three lines of experimental evidence: (1) the quality of color of solutions, of less than 0.01% concentration, changes with greater dilution,[2] (2) certain chromates crystallize with water;[3] (3) colorimetric studies of sensitiveness of color at these lower concentrations indicate *two maxima.*[4]

In respect to the first, in accordance with Beer's law and the teaching

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[1] Walden, *Z. physik. Chem.*, **2**, 73.

[2] *Vide infra.* Also note application of Beer's law.

[3] Groger, *Z. anorg. Chem.*, **70**, 143; cf. Schulze, *Ibid.*, **10**, 154; Briggs, *Ibid.*, **56**, 254. For hydration addition-products of metallic dichromates, see Barbieri and Lanzoni, *Atti accad. Lincei*, **19**, 584; **20**, 119, 1161. Compare also: $Na_2Cr_2O_7.2H_2O$, $Na_2CrO_4.10H_2O$, $MgCrO_4.7H_2O$.

[4] *Am. Chem. J.*, **35**, 255; **36**, 198, 516.

$$\begin{array}{llcllcllcl}
 & \text{Neut. and hydration.} & & \text{Hydrolysis.} & & & \text{Ionization.} & & & \text{Ionization} \\
 & 4CrO_4 + H_2O & \rightleftarrows & H_2Cr_4O_{13} & + KOH & \rightleftarrows & HCr_4O_{13} + H & & & Cr_4O_{13} + 2H \\
 & & & \uparrow H_2O & & & & & & \\
\text{I} & (a)\ 4CrO_3 + KOH & \rightleftarrows & KHC_4O_{13} & & \rightleftarrows & HCr_4O_{13} + K & & \rightleftarrows & Cr_4O_{13} + K + H \\
 & & & \uparrow H_2O & & & & & & \\
 & (b)\ 4CrO_3 + 2KOH & \rightleftarrows & K_2Cr_4O_{13} & + H_2O & \rightleftarrows & KCr_4O_{13} + K & & \rightleftarrows & Cr_4O_{13} + 2K \\
 & (a)\ 3CrO_3 + KOH & \rightleftarrows & KHCr_3O_{10} & & \rightleftarrows & HCr_3O_{10} + K & & \rightleftarrows & Cr_3O_{10} + K + H \\
\text{II} & & & \uparrow H_2O & & & & & & \\
 & (b)\ 3CrO_3 + KOH & \rightleftarrows & K_2Cr_3O_{10} & + H_2O & \rightleftarrows & KCr_3O_{10} + K & & \rightleftarrows & Cr_3O_{10} + 2K \\
 & (a)\ 2CrO_3 + KOH & \rightleftarrows & KHCr_2O_7 & & \rightleftarrows & HCr_2O_7 & & \rightleftarrows & Cr_2O_7 + K + H \\
\text{III} & & & \uparrow H_2O & & & & & & \\
 & (b)\ 2CrO_3 + 2KOH & \rightleftarrows & K_2Cr_2O_7 & + H_2O & \rightleftarrows & KCr_2O_7 + K & & \rightleftarrows & Cr_2O_7 + 2K \\
 & (a)\ CrO_3 + KOH & \rightleftarrows & KHCrO_4 & & \rightleftarrows & HCrO_4 + K & & \rightleftarrows & CrO_4 + K + H \\
\text{IV} & & & \uparrow H_2O & & & & & & \\
 & (b)\ CrO_3 + 2KOH & \rightleftarrows & K_2CrO_4 & + H_2O & \rightleftarrows & KCrO_4 + K & & \rightleftarrows & CrO_4 + 2K
\end{array}$$

of Hantzsch,[1] we would expect (*a*), (*b*) and (*c*) above to represent three different chromophores and to give closely related but different colors. This is shown in the colors of low-concentrated solutions and is further supported by variations of color of hydrated chromates.

In respect to the second, Groger[2] prepared five salts of the composition: (*a*) $4\ ZnO.CrO_3.3H_2O$; (*b*) $3\ ZnO.CrO_3.2H_2O$; (*c*) $4\ ZnO.2CrO_3.3H_2O$; (*d*) $ZnO.2CrO_3.H_2O$; (*e*) $ZnO.CrO_3.H_2O$. These varied in color and were stable only in greater dilutions than (*a*) 0.114, (*b*) 0.666, (*c*) 1.92, (*d*) 4.62, (*e*) 4.62 + molal concentrations, respectively. All these formulas can not only be made to conform to the above indicated hydration-forms of mono- and di-chromic acid[3] but, as was shown by Groger, the more complicated are stable only in the more dilute aqueous solutions. Furthermore, Groger[4] found that $ZnCrO_4.H_2O$ contained, not water of crystallization, but water of composition. In respect to the third, Horn[5] has shown that in colorimetric readings of solutions of potassium chromate in varied concentrations, two maxima of sensitiveness[6] are found which he was unable to explain. These are shown in a curve[7] and are indicated in the following condensed table:

G. at. wt Cr in l's.	Recalc. as % Cr.	Sensitiveness.	G at. wt. Cr in l's.	Recalc. as % Cr	Sensitiveness
250	0.0208	0.07	8000	0.0006	250.00*
500	0.0104	0.34	9900	0.0005	50.00
667	0.0078	0.69	10667	0.0004	33.33
1000	0.0052	1.45	16000	0.0003	25.00
2000	0.0026	3.59	17700	0.0003	100.00
3600	0.0014	33.33	32000	0.00013	333.33*
4000	0.0013	100.00	110000	0.00005	25.00
7500	0.0007	100.00	150000	0.00003	33.33

Here it will be observed that the two maxima of sensitiveness are found far below the dichromate-chromate transition-concentration.[8] An assumption of hydration could involve only two chromophoric changes and only two were found by Horn. Of course, had he carried his readings to higher concentrations he would have found other maxima, as at the transition-concentrations of $H_2CrO_4 \rightleftarrows H_2Cr_2O_7 \rightleftarrows H_2Cr_3O_{10}$, etc. He found only one maximum each for solutions of copper sulfate[1] and ammoniacal copper sulfate.[2] This is to be expected,[3] since copper, a bivalent kation, could yield only two chromophores, the kation and the hydrated form.

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[1] *Z. physik. Chem.*, **63**, 367, 377.

[2] *Z. anorg. Chem.*, **70**, 135; see also *Ibid.*, **54**, 185.

[3] See studies on the decomposition of hydrated ammonium salts, THIS JOURNAL, **29**, 1137.

[4] *Z. anorg. Chem.*, **70**, 143.

[5] *Am. Chem. J.*, **35**, 255; **36**, 195, 516.

[6] Horn defines sensitiveness as the "reciprocal of the weight in milligrams of the colored solute that produces that change in color that can just be differentiated with certainty."

[7] *Am. Chem. J.*, **36**, 198.

[8] *Vide infra.*

In accordance with Weber's law of sensation, it is to be expected that solutions involving a single chromophore will require increased quantities of solute molecules to produce a definite sensation of change of color. Now, since Horn has demonstrated that, at certain concentrations, some solutions do not require logarithmic increments of colored solute molecules to produce a sensation of change, it may be assumed that: (1) the eye varies in sensitiveness for different concentrations or; (2) the eye functionates according to the logarithmic series and that *the solutions themselves involve chromophoric changes.* The latter hypothesis seems the more probable, since some solutions,[4] for instance, solutions of potassium chromate containing much free alkali and in greater concentrations than studied by Horn, seem to follow Weber's law.

From the foregoing it seems safe to assume that *hydration of colored molecules or colored ions produces chromophoric changes.*

The hydration of chromates may yield only two forms; the polychromates may yield a greater number. Without involving hydrolysis or the formation of stereo-isomeric forms, it can be shown, theoretically, that dichromic acid may have five forms; trichromic acid, seventeen forms; tetrachromic acid, thirty-six forms; chromic oxide, nineteen forms. Of course, most of these seventy-seven forms are impossible since hydrolysis is more probable than hydration in most solutions—yet, since in most studies of chromate solution assumptions of hydration have been neglected, limited data have been taken and contradictory conclusions have been drawn.

Investigations of solutions of chromic oxide, dichromates and chromates have been made by methods of electrical conductivities,[5] cryoscopic methods,[1] ebullioscopic methods,[2] optical absorption methods,[3] colorimetric methods,[4] speed of reaction with iodide-iodate solutions,[5] speed of hydrolysis of ethyl acetate,[6] of diazo acetic ester,[7] catalysis of hydrogen peroxide,[8] solubilities of difficultly soluble chromate salts,[9] etc.[10] All these methods, though invaluable, may involve errors of interpretation if recog-

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[1] *Am. Chem. J.*, 36, 195.

[2] *Ibid.*, 36, 517.

[3] An investigation of these solutions by the method of this contribution will be made.

[4] A search will be made in this laboratory for a strictly *monochromic solution, i. e.*, one that conforms to Weber's law, and yields only one chromophore.

[5] Walden (*Z. physik. Chem.*, 1, 529; 2, 70) measured the conductance of chromate solutions at 25° and found: that the salts of $H_2Cr_2O_7$ are less stable but are better conductors than isomorphous sulfates; salts of $MHCrO_4$ do not exist, di- and tri-chromates are hydrolyzed to dichromate and chromate. For further discussion of Walden's studies *vide infra.*

Whetham (*Proc. Roy. Soc.*, 71, 382) studied the conductance of $^1/_2K_2Cr_2O_7$ at 0° and obtained for molal concentrations of 0.00001, 0.0001, 0.001, 0.01 and 0.1, respectively, 0.991, 0.929, 0.870, 0.858, and 0.783—fractions of conductance at infinite dilution. Costa (*Gazz. ital. chim.*, 36, 535) studied the conductance of chromic acid at 0° and concluded that, in solutions not too concentrated, the formula is $H_2Cr_2O_7$.

Lundberg (*Z. anorg. Chem.*, 55, 426) found in $N/10$ solution of K_2CrO_4 a 0.012%

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hydrolysis and in $N/10$ solution of $K_2Cr_2O_7$ a 0.094% ionization as $HCrO_4 \rightleftarrows H + CrO_4$.

Sherrill and Merrill (THIS JOURNAL, **29**, 1650) measured the conductance of ammonium chromate in the presence of an excess of ammonium hydroxide and concluded that at 18° in 0.0025 solution, chromic acid existed in the equilibrium:

$$H_2CrO_4 \rightleftarrows H + HCrO_4.$$

[1] Ostwald (*Z physik. Chem.*, **2**, 78) made cryoscopic molecular weight determinations of chromic acid and concluded that the formula is $H_2Cr_2O_7$. He gives as confirmatory evidence for this conclusion: (*a*) salts like K_2CrO_4 are alkaline, whereas aqueous solutions of chromic acid are good conductors, (*b*) the color of dichromates agrees completely with the color of aqueous solutions of CrO_3. This latter statement is completely refuted by the experiments of this contribution.

Sherrill and Eaton (THIS JOURNAL, **29**, 1642) determined the van't Hoff factors for $K_2Cr_2O_7$ and $H_2Cr_2O_7$ in various concentrations.

[2] Costa (*Gazz. chim. ital.*, **36**, 535) concluded that the formula of chromic acid in aqueous solutions is $H_2Cr_2O_7$.

[3] Sttetegast (*Wied. Ann.*, **7**, 242). Hantzsch and Clark (*Z physik. Chem*, **63**, 367) studied absorption-spectra of various chromates and concluded that they are identical in cases of: (*a*) $CrO_3 + H_2O$; $K_2CrO_4 + H_2SO_4$; $K_2Cr_2O_7 + H_2SO_4$; (*b*) $K_2CrO_4 + H_2O$; $K_2CrO_4 + KOH$; $K_2CrO_4 + CH_3OH$. Their experiments tended to show that (*a*) and (*b*) differed—in pure water the behavior of the dichromate diverges slightly in the direction of the chromate and *vice versa*. For further discussion of Hantzsch and Clark's data, see below.

[4] Horn and Blake (*Am. Chem. J.*, **35**, 253; **36**, 195, 516) made colorimetric studies of sensitiveness of reading of potassium chromate solutions. See discussion on pages following.

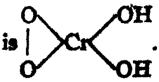
[5] Lundberg (*Z. anorg. Chem.*, **55**, 426) obtained data too irregular to enable them to decide between the two contested equations: (*a*) $CrO_4^{--} + H_2O \longrightarrow HCrO_4^{-} + OH^{-}$, (*b*) $2CrO_4^{--} + H_2O \longrightarrow Cr_2O_7 + 2OH^{-}$.

[6] Sand and Kastle (*Ibid.*, **52**, 101) concluded that at 25° hydrolytic dissociation to the extent of 0.18% takes place according to the reaction: $Cr_2O_7 + H_2O \longleftrightarrow 2CrO_4 + 2H$. See also Abegg and Cox (*Ibid.*, **48**, 425) who held that the Cr_2O_7 ion splits completely into CrO_4 and CrO_3 in solutions of moderate strength.

[7] Spitalsky (*Ibid.*, **53**, 184; **54**, 265; **56**, 72; **69**, 179).

[8] Beck and Stegmüller (*Z. Electrochem.*, **17**, 843; *Arb. Kais. Gesundheitsamt.*, **34**, 446). Sherrill and Russ (THIS JOURNAL, **29**, 1661) showed that at constant temperature the solubilities vary directly as the hydrogen ion except in the case of $PbCrO_4$, which in concentrated solution was equal nearly to the square of the hydrogen ions.

[9] Abegg and Cox (*Z. physik. Chem.*, **48**, 725) maintain that hydrolytic dissociation to a limited extent takes place as follows: $Cr_2O_7 + H_2O \longrightarrow 2CrO_4 + 2H$.

[10] For thermochemical investigations see Sabatier, *Compt. rend.*, **103**, 138, 267. Manchot (*Ber.*, **36**, 4305; **39**, 1352, 3512) made oxidation experiments and concluded that the formula of chromic acid is  .

nition of the influence of dilution, temperature, and quantities of acids or alkalies present, are not taken into consideration. The limitations of some of these investigations will be indicated in the following discussions.

Method of Colorimetric Study.

Solutions of (*a*) chromic acid, (*b*) potassium dichromate, (*c*) potassium chromate, (*d*) sodium chromate, (*e*) potassium chromate plus one molecule of potassium hydroxide, (*f*) potassium chromate plus six molecules of potassium hydroxide were put up in square, uniformly sized bottles of clear glass and 39 mm. cross-section.[1] Solutions were prepared in concentrations from saturation down to 0.0001%, calculated as H_2CrO_4. The respective tenths of the following concentrations were prepared:

10, 1.0, 0.01, 0.001, 0.0001, 0.00001

These percentage-concentrations, instead of fractional normal solutions, were prepared (1) because they gave a better basis of comparison than the latter, and (2) all the solutions in low and equal concentrations gave the same color—which is yellow and is assumed to be that of H_2CrO_4.

Any two series were compared and were found to differ in the upper ranges when concentrations were the same; or, by varying the concentrations of two series, colors could be matched evenly, thus indicating *different tinctorial power for equal concentrations.*

Only single bottles from the different series were matched, not only for the reason that the colors could usually be matched as closely as necessary, but for the more important reason that the method of reading the bottles *in tandem* of two or more involves errors. The most important observation of this contribution is that *color-changes result from dilution* of dichromates, etc. Therefore, when the *tandem* method is employed, the mass of solute-molecules, assumed to be the same when viewed in equal-color solutions, really are contained in two or three volumes and since hydrolysis results, only approximate values are obtained. When necessary other concentrations than the ones indicated above were prepared. All the solutions were prepared with distilled water, and the very dilute solutions were prepared with ammonia-free water. The following series were prepared and compared at ordinary temperatures (15–25°):

I. $K_2CrO_4 : K_2Cr_2O_7$
II. $K_2Cr_2O_7 : H_2Cr_2O_7(CrO_3 + H_2O)$
III. $K_2CrO_4 : K_2CrO_4 + KOH$
IV. $K_2CrO_4 : K_2CrO_4 + 6KOH$

In Table I the first column gives the molar concentrations of the chromate; the second, the percentages of concentration of the chromate; the third, the percentage-concentration of the dichromate just matching the color of the chromate; the fourth, the ratio of concentration of the

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[1] See THIS JOURNAL, 36, 407 (1914).

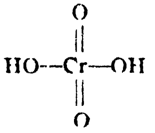
TABLE I.

Liters containing 52 g. of Cr.	K_2CrO_4 as % of H_2CrO_4.	$K_2Cr_2O_7$ as % of H_2CrO_4.	Color ratio.	$K_2Cr_2O_7$ in "$K_2Cr_2O_7$."	Liters containing 52 g. of Cr.	K_2CrO_4 as % of H_2CrO_4.	$K_2Cr_2O_7$ as % of H_2CrO_4.	Color ratio.	$K_2Cr_2O_7$ in "$K_2Cr_2O_7$."	Liters containing 52 g. of Cr.	K_2CrO_4 as % of H_2CrO_4.	$K_2Cr_2O_7$ as % of H_2CrO_4.	Color ratio.	$K_2Cr_2O_7$ in "$K_2Cr_2O_7$."
0.4070	29	0.16	181.2	100.60	1.073	11	0.09	122.2	67.33	39.34	0.30	0.024	12.50	6.89
0.4215	28	0.16	175.0	96.67	1.180	10	0.08	117.6	64.78	47.31	0.25	0.024	10.40	5.72
0.4370	27	0.15	168.7	93.17	1.390	9	0.08	112.5	61.95	59.01	0.20	0.023	8.69	4.82
0.4539	26	0.15	173.3	95.72	1.474	8	0.08	100.0	55.00	76.68	0.15	0.022	6.82	3.78
0.4721	25	0.15	166.6	92.00	1.686	7	0.08	87.5	48.06	118.0	0.10	0.022	4.54	2.51
0.4917	24	0.14	171.4	94.67	1.967	6	0.07	85.7	47.06	139.0	0.09	0.021	4.28	2.37
0.5131	23	0.14	164.3	90.72	2.360	5	0.06	83.3	45.72	147.4	0.08	0.020	4.00	2.21
0.5365	22	0.13	169.2	93.50	2.950	4	0.06	66.6	36.45	168.6	0 07	0.019	3.68	2.03
0.5620	21	0.13	161.5	89.17	3.934	3	0.05	60.0	32.78	196.7	0.06	0.017	3.52	1.95
0.5901	20	0.12	161.6	89.22	4.917	2.5	0.045	55.5	30.28	236.0	0.05	0.016	3.20	1.77
0.6210	19	0.11	172.7	95.39	5.901	2.0	0.040	44.4	24.11	295.0	0 04	0.015	2.66	1.47
0.6557	18	0.11	163.6	90.33	11.800	1.0	0.035	28.6	15.33	393.4	0.03	0.014	2.15	1.19
0.6942	17	0.10	170.0	93.89	13.900	0.9	0.022	25.7	13.72	590 1	0.020	0.012	1.67	0.92
0.7376	16	0.10	160.0	88.34	14.740	0.8	0.022	22.8	12.11	786.8	0.015	0.010	1.50	0.83
0.7868	15	0.10	150.0	82.78	16.860	0.7	0.035	20.0	11.05	1180.0	0.010	0.010	1.00	0.00
0.8430	14	0.095	147.4	81.33	19.670	0.6	0.035	17.1	9.45	1390.0	0.009	0.009	1.00	0.00
0.9078	13	0.090	144.4	79.66	23 600	0.5	0.030	16.7	9.22	1474.0	0.008	0.008	1.00	0.00
0.9835	12	0.090	133.3	73.50	29 500	0 4	0.025	16.0	8.83	1686.0	0.007	0.007	1.00	0.00

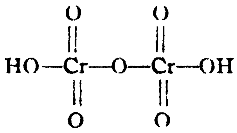
chromate and the dichromate; the fifth, the calculated per cent. of dichromate which really is in the chromophoric form $K_2Cr_2O_7$.

It may be observed in the table that: (1) in concentrations below 0.01%, the compared solutions are identical in color, which is some shade of yellow; (2) above this concentration the color of the dichromate becomes tinged with red, while the chromate remains yellow; (3) at higher concentrations both solutions are tinged with red but differ widely in *intensity of color*, as is shown by the different concentrations necessary to duplicate the colors.

The color ratio was obtained by dividing the respective concentrations of dichromate by the corresponding color-matched concentrations of chromate. Thus, for instance, 29% of the latter possesses the same color as a 0.16% solution of the former, a ratio of concentration equal to 181.1:1. If it is assumed that only two chromophores are present:



$\mathrm{HO{-}Cr({=}O)_2{-}OH}$



$\mathrm{HO{-}Cr({=}O)_2{-}O{-}Cr({=}O)_2{-}OH}$

then the latter is 181.1 times as intensely colored as the former. That this maximum color-ratio is nearly correct for concentrated solutions was corroborated by diluting a solution of 68 g. of sodium chromate to 100 cc. and finding that it (48.54% H_2CrO_4) was matched by a 0.27% solution of potassium dichromate, a color-ratio of 183.5; also by a 0.2% solution of chromic acid or a color-ratio of 247.7. If it is assumed that the chromate-dichromate ratio is 180, from the data obtained, actual quantities of chromate and dichromate in the "dichromate" solutions can be calculated. Since at certain concentrations (as below 0.01%) of both chromate and dichromate the colors are identical,[1] it may be assumed that the chromium present in both is in the same chromophoric form. But if all the chromate at these low concentrations were transformed to dichromate, it would be approximately 183.5 times more colored than it is. At higher concentrations more and more dichromate is formed, but unchanged chromate also is present and this, if transformed to dichromate, would raise the color-ratio to 183.5. Therefore, at any concentration, the percentage of dichromate in the chromate-dichromate mixture is equal to the color-ratio minus one, multiplied by 100 ÷ 183.5. In the fifth column of the table, 180 was used as the factor instead of 183.5. Since dichromates are acid in reaction, thus indicating the presence of free "chromic acid," which is more strongly colored than dichromates, the correctness of factor 180 can not be strictly maintained, though it probably is approximately correct.[1]

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[1] For the above-indicated reasons, in solutions of 0.01 to 0.05% concentrations of chromate, difficulty was met with in matching colors. The densities of color, rather than the quality of color, were compared. Above 0.05% and below 0.01% the solutions gave no difficulty in reading.

Sherrill[2] states that "in a 0.1 molal solution of potassium dichromate approximately 15% of the salt exists as hydrochromate and 85% as dichromate, while in a 0.01 molal solution approximately 45% exists in the former state." Now, 0.1 and 0.01 molal solutions of dichromate contain 52 g. of chromium in 20 and 200 liters, respectively. As seen in the table, 15 and 45% of dichromate are contained in 107.29 and 147.53 liters, respectively. These approximations of values are interesting not only for the reason that Sherrill[3] claimed no great accuracy, but also for the reason that he obtained his data by solubility experiments with silver chromate and dichromate.[4]

The Transition-Concentration of Chromates and Dichromates.

A study of Table I shows that at 0.01 and 0.10 concentrations at ordinary temperatures, chromates are transformed to dichromates—in other words, the mass action of water[5] below these concentrations completely transforms dichromate to chromate.

Walden[6] observed at 25°, in these same concentrations, abnormal electrical conductivities, which he could not explain. These are indicated by the asterisks in the following condensed table.

Liters containing 52 g. of Cr.	Recalc. as % of H_2CrO_4.	As 1/2 molecules each of							
		$K_2Cr_2O_7$.		$K_2Cr_3O_{10}$.	$2H_2CrO_4$.	K_2CrO_4.		$Na_2Cr_2O_7$.	
		μ.	10^3 Δl/l.	μ.	μ.	μ.	10^3 Δl/l.	μ.	10^3 Δl/l.
32	0.3687	114.4	..	275.9	347.1	121.2	.	95.0	..
64	0.1843	116.6	1.830	282.9	354.7	127.5	5.20	96.5	1.580
128	0.0922	117.6	0.858	286.1	358 9	132.2	3.69	96.8	0.310
256	0.0461*	118.0	0.340*	286.4*	361.3*	136.1	2.95	97 0	0.207*
512	0.0230	118.7	0.593	234.4	360.8	138.7	1.91	97.7	0.722
1024	0.0115	120.7	1.850	278.2	358.4	140.7	1.44	98.8	1.130
2048	0.0057	124.1	2.650	..	353.7	...	..	102.8	3.540

Two important observations are made: (1) potassium chromate does not show abnormal conductivities within the range of concentations studied by Walden; (2) the others, all di- or tri-chromates, show abnormal conductivities at 0.046% concentrations, *i. e.*, at the concentration wherein much transition[1] takes place according to the reaction:

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[1] See curves on pages following.

[2] THIS JOURNAL, 29, 1674.

[3] Sherrill is the first investigator to recognize the $K_2CrO_4 \rightleftarrows K_2Cr_2O$ equilibrium in solutions of both chromates and dichromates.

[4] Abegg and Cox (*Z. physik. Chem.*, 48, 425) considered that a dichromate solution contains mainly CrO_4'' ions and undissociated K_2CrO_4, while the concentration of Cr_2O_7'' ions is small. See Spitalsky (*Z. anorg. Chem.*, 53, 184; 54, 265) for opposite view. See also Lundberg, *Ibid.*, 55, 426.

[5] Sherrill and Eaton (THIS JOURNAL, 29, 1642). "If the dichromate ion becomes hydrated to form the hydrochromate ion, the condition most favorable for its formation would be in the more dilute solutions, according to the mass-action law."

[6] *Z. anorg. Chem.*, 1, 546; 2, 70.

$$H_2Cr_2O_7 + H_2O \rightleftarrows 2H_2CrO_4.$$

From spectra-absorption studies Hantzsch and Clark[2] obtained the following data:[3]

($K_2Cr_2O_7$ + *n*-Mols Acid ($\lambda = 486\ \mu\mu$)).

v.	Recalc. as % H_2CrO_4	In pure H_2O.	N/2000 CH_3COOH.	N/H_2SO_4.	N/10 H_2SO_4.	In 99% H_2SO_4
100	0.2360	88.7	90.9	90.9	90.5	91.4
200	0.1180	87.0	90.0*	88.8*	90.0*	90.5*
500	0.0472	86.8*	90.4	89.3	90.7	90.7
1000	0.0236	87.2	. .	90.4	91.2	91.2
2000	0.0118	87.6	. .	91.0		

Here as before it is observed: (1) that abnormal phenomena occur at 0.047% concentrations; (2) acid solutions require higher concentrations; (3) the data, instead of indicating no chromophoric variation,[4] correlate with the conclusions of this contribution.

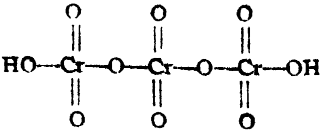
The Mass of Water Dissociating Dichromates.

Since a 0.01% concentration of potassium dichromate (calculated as per cent. of H_2CrO_4) is completely hydrolyzed to monochromate, 294.2 g. of it will be hydrolyzed by 2,360,400 g. of water or one molecule of potassium dichromate will be hydrolyzed by 131,000 molecules of water. Since two molecules of alkali transform dichromates to chromates *one molecule of alkali and 65,000 molecules of water have the same dissociating effect on dichromates.*

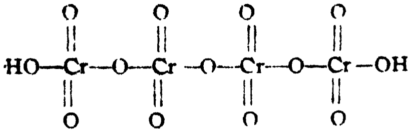
The Dichromate-Chromic Acid Color-Ratios.

In the manner described above the data of Table II were obtained.

These experiments show that, for equal concentrations of chromium, *chromic acid solutions are more colored than dichromate solutions.* This can be accounted for either on the basis that the dichromate is more largely dissociated into the less-colored monochromate, or that the *chromic acid is associated in more colored structures* as:



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-OH$$



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-OH$$

either of which structure is more deeply colored[5] than the dichromate. That the latter view is the more probable follows from the fact that,

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[1] Cf. data on pages following.

[2] *Z. physik. Chem.*, 63, 373.

[3] Cf. Sabatier, *Compt. rend.*, 103, 49, 138, 267.

[4] See the contrary conclusions of Hantzsch and Clark, *Z. physik. Chem.*, 63, 373.

[5] Hantzsch and Clark, *Z. physik. Chem.*, 63, 377.

TABLE II.

$CrO_3 : K_2Cr_2O_7$.						$CrO_3 : K_2CrO_4$.					
CrO_3 as % of H_2CrO_4.	$K_2Cr_2O_7$ as % of H_2CrO_4.	Color-ratio.	CrO_3 as % of H_2CrO_4	$K_2Cr_2O_7$ as % of H_2CrO_4.	Color-ratio.	CrO_3 as % of H_2CrO_4.	K_2CrO_4 as % of H_2CrO_4.	Color-ratio.	CrO_3 as % of H_2CrO_4.	K_2CrO_4 as % of H_2CrO_4.	Color-ratio.
5.0	13.0	2.60	0.500	0.6000	1.20	0.100	16.00	160.0	0.0060	0.0080	1.25
4.5	12.0	2.66	0.400	0.5000	1.20	0.090	12.00	133.0	0.0050	0.0070	1.40
4.0	9.0	2.25	0.080	0.1000	1.25	0.080	10.00	125.0	0.0045	0.0050	1.11
3.5	7.0	2.00	0.060	0.0700	1.16	0.070	8.00	114.0	0.0040	0.0042	1.05
3.2	6.0	1.87	0.050	0.0600	1.20	0.060	6.50	108.0	0.0040	0.0041	1.02
3.0	5.4	1.80	0.035	0.0400	1.14	0.050	5.00	100.0	0.0030	0.0030	1.00
2.9	5.0	1.72	0.008	0.0090	1.12	0.040	3.00	75.0	0.0020	0.0020	1.00
2.5	4.0	1.60	0.007	0.0080	1.14	0.030	0.50	17.0	0.0010	0.0010	1.00
1.3	2.0	1.54	0.006	0.0070	1.16	0.020	0.10	5.0	0.0009	0.0009	1.00
1.0	1.4	1.40	0.004	0.0045	1.12	0.010	0.04	4.0	0.0008	0.0008	1.00
0.8	1.0	1.25	0.003	0.0030	1.00	0.009	0.03	3.3	0.0007	0.0007	1.00
0.7	0.9	1.28	0.002	0.0020	1.00	0.008	0.02	2.5	0.0006	0.0006	1.00
0.65	0.8	1.23	0.001	0.0010	1.00	0.007	0.01	1.1	0.0005	0.0005	1.00

in 0.2% solutions, the dichromate seems to reach a maximum color-ratio of 180, while the chromic acid is somewhat darker (color-ratio, 225) than the dichromate at this concentration, but steadily increases in higher concentrations until its color-ratio is twice that of the dichromate.

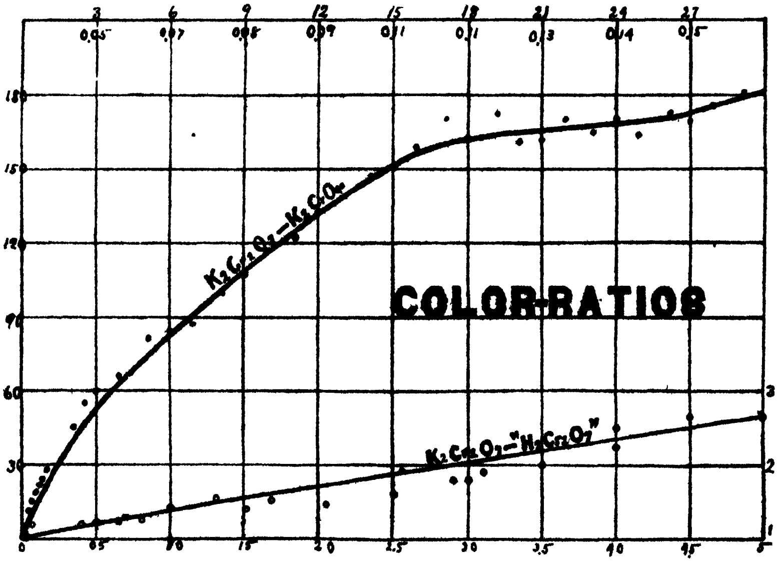

Plate I.

These curves were plotted from the data of Tables I and II. The ordinates are color-ratios; the abscissas are concentrations. It will be observed that the potassium dichromate indicates two phases in concentrations above 0.01%—(1) from 0.01 to 0.1% concentrations, the true dichromate phase; (2) above 0.1% probably[1] the trichromate phase, and possibly the tetrachromate phase.

The data of various investigators[2] tend to prove the existence in aqueous solutions of dichromic acid[3] only—the existence of tri-, tetra-, and monochromic acids were doubted.[4] Since only moderately[5] concentrated solutions were employed, most data pointed to the existence of the dichromic acid only.

Sherrill and Eaton[6] made cryoscopic determinations of potassium dichromate and chromic acid solutions and calculated the van't Hoff factors, which are 3 for $K_2Cr_2O_7 \rightleftharpoons 2K + Cr_2O_7$, and 4 for $2KHCrO_4 \rightleftharpoons 2K + 2HCrO_4$. The following quoted data have been condensed:

K_2CrO_7			$H_2Cr_2O_7$		
Molal conc in 1 liter.	Recalc as % of H_2CrO_4	van't Hoff factor	Molal conc in 1 liter.	Recalc. as % of H_2CrO_4	van't Hoff factor.
0.05340	1.2650	2.66	0.10160	2.398	2.91
0.04000	0.9440	2.74	0.07670	1.810	2.89
0.03680	0.8686	2.79	0.07180	1.695	2.92
0.02880	0.6819	2.88	0.06440	1.520	2.90
0.02760	0.6515	2.94	0.05880	1.388	2.90
0.02053	0.4839	2.98	0.04690	1.107	2.96
0.01743	0.4114	3.04	0.03340	0.788	3.06
0.01384	0.3267	3.16	0.02730	0.644	3.07
0.01105	0.2608	3.28	0.01370	0.323	3.26
0.00510	0.1204	3.70	0.00958	0.226	3.33

These data seem to prove that: (1) in very concentrated solutions both the dichromate and the chromic acid are incompletely ionized; (2) at about 0.4% concentration, the dichromate predominates; and (3) in very dilute solutions, the chromate predominates. However, if van't Hoff factors for all the chromic acids are calculated, we obtain the following:

$$H_2Cr_4O_{13} \rightleftharpoons 2H + Cr_4O_{13} \quad \ldots\ldots\ldots\ldots \quad 3(1.5)$$
$$H_2Cr_3O_{10} + H_2CrO_4 \rightleftharpoons 4H + Cr_3O_{10} + CrO_4 \ldots\ldots\ldots\ldots \quad 6(2)$$
$$2H_2Cr_2O_7 \rightleftharpoons 4H + 2Cr_2O_7 \ldots\ldots\ldots\ldots \quad 6(3)$$
$$4H_2CrO_4 \rightleftharpoons 8H + 4CrO_4 \ldots\ldots\ldots\ldots \quad 12(6)$$

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[1] Experiments with more soluble sodium dichromate and chromic acid by the methods of this contribution and other physical-chemical methods, to determine the presence of trichromic and tetrachromic acid phases in solutions of chromic oxide, will be undertaken in this laboratory.

[2] See résumé above.

[3] Costa's (*Gazz. ital. chim.*, **36**, 535) molecular-weight determinations by the boiling-point method, with quite concentrated solutions of chromic oxide, indicated its tendency to yield polychromates.

[4] See especially Walden, *Z. physik. Chem.*, **2**, 73.

[5] See especially Hantzsch and Clark, *Ibid.*, **63**, 373.

[6] THIS JOURNAL, **29**, 1645.

Here it may be seen that factors less than 3 may *not only indicate non-ionized molecules of the dichromate but also the formation of polychromates.*

The Influence of an Excess of Alkali on Chromates.

Since potassium chromate is alkaline in reaction, thus indicating hydrolysis:

$$(a)\ K_2CrO_4 + H_2O \rightleftarrows KHCrO_4 + KOH$$

and since, in concentrated solutions, it undergoes condensation:

$$(b)\ 2K_2CrO_4 + H_2O \rightleftarrows K_2Cr_2O_7 + 2KOH$$

thus, in both cases yielding free alkali, it may be expected to give color-variations in the presence of different quantities of free alkali. This conclusion was verified by experiment.

$K_2CrO_4 + KOH$.			$K_2CrO_4 + 6KOH$.		
K_2CrO_4 as % of H_2CrO_4.	$K_2CrO_4 + KOH$ as % of H_2CrO_4.	Color-ratio.	K_2CrO_4 as % of H_2CrO_4.	$K_2CrO_4 + 6HOH$ as % of H_2CrO_4.	Color-ratio.
13.0	23.0	1.78	5.5	8.0	1.45
12.6	19.0	1.51	5.0	7.0	1.40
12.0	17 0	1.42	4.3	6.0	1.39
11.0	15.0	1.36	4.0	5.0	1 25
8.4	10.0	1.19	3.4	4.0	1.11
7.3	8.0	1.09	3.0	3.0	1.00
7.0	7.5	1.07	2.0	2.0	1.00
7.0	7.0	1.00	1.0	1.0	1.00
1.0	1.0	1.00	0.08	0.08	1.00

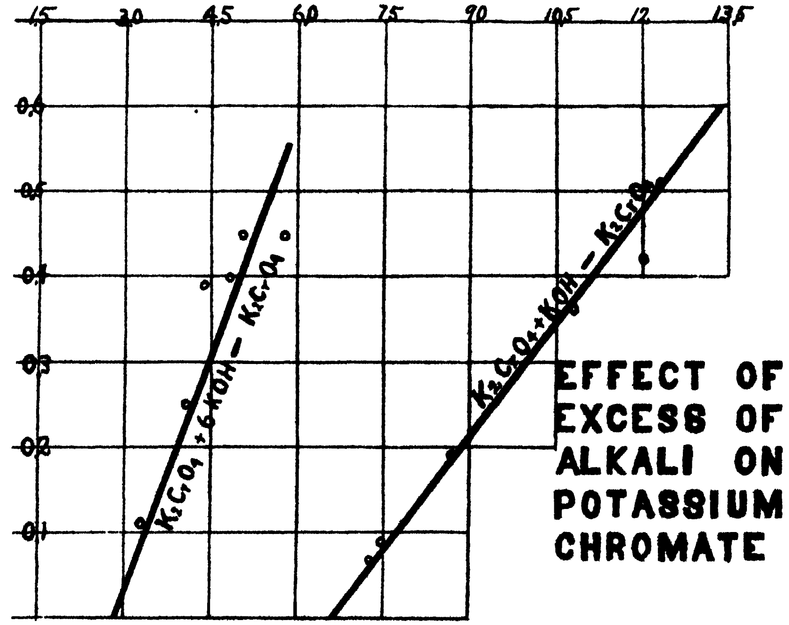

Plate II.

These experiments show that: (1) definite color-variations are caused by an excess of alkali; (2) solutions of potassium chromate containing one molecule of alkali match the solutions containing only potassium chromate up to 7% concentrations; (3) solutions containing six molecules of alkali match the chromate solutions only up to 3% concentrations. This divergence at lower concentrations for the latter is to be expected, since, being more nearly *monochromic* than either of the other two solutions, it will show a color-difference throughout a wider range of concentrations.

These studies with alkali show that in moderately concentrated solutions *chromates contain an appreciable quantity of dichromate,*[1] at least in solutions more concentrated than 3%. By the use of the color-factor 180, and on the basis that the color-variations are caused by chromophoric changes as indicated in equation (*b*) above, it may be calculated that a 5% solution of "potassium chromate" contains chromate and dichromate in the ratio of 450 : 1. Of course, more concentrated solutions contain more and more of the dichromate.

The Influence of Heat on Chromate Solutions.

Heating solutions of chromic acid, potassium dichromate, potassium chromate, and potassium chromate containing alkali, gives marked deeping of the colors. This phenomenon is difficult to explain except on the basis of dehydration change of chromophores in accordance with·

$$H_2CrO_4 \rightleftarrows H_2Cr_2O_7 \rightleftarrows H_2Cr_3O_{10} \rightleftarrows H_2Cr_4O_{13}.$$

The following table includes data obtained by heating towel-covered bottles for 20 minutes in the steam of vigorously boiling water baths, and making immediate comparisons with room-temperature samples.

The first column indicates concentrations as per cent. of H_2CrO_4; the second columns, marked (*b*), the readings at ordinary temperatures against equal colored dichromate solutions; the columns marked (*at*) and (*bt*), the readings of chromic acid and dichromate solutions matching the

TABLE IV.

Chromic acid (*a*)							$K_2Cr_2O_7$ (*b*)		
Per cent.	*at.*	*r*	Per cent	*b*	*bt*	*r.*	Per cent	*bt*	*r*
4.000	20+	5+	2 30	4 00	15.00	3.7	4.00	15 000	3 7
3.000	15.00	5.0	1.00	1 40	5.00	3.7	2 00	7.000	3.5
2.000	8.00	4.0	0.70	0.90	3 00	3.3	1.00	3 500	3.5
1.500	5.00	3.3	0.60	0.70	2.00	2.9	0 60	2 000	3.3
0.800	2.00	2.5	0.20	0 20	0.40	2.0	0 20	0 500	2.5
0.500	1.00	2.0	0.10	0 14	0 20	1.5	0 06	0 100	1 6
0 050	0 08	1.6	0 05	0 06	0.09	1 3	0 01	0 015	1 5
0.009	0 01	1 1	0.02	0 03	0 04	1 3	0 0007	0 0008	1 1

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[1] See Hantzsch and Clark, *Z. physik. Chem*, 63, 374; Merrill, THIS JOURNAL, 29, 1650, 1661

K_2CrO_4 (*c*).				K_2CrO_4 + KOH (*d*).				K_2CrO_4 + 6KOH.			
Per cent.	*b.*	*bt.*	*r.*	Per cent	*b.*	*bt.*	*r*	Per cent.	*b.*	*bt.*	*r.*
29.0	0.16	0.80	5.0	19.0	0.09	0.600	6.5	8.0	0.065	0.40	6.1
20.0	0.12	0.55	4.5	10.0	0.08	0.300	3.7	4.0	0.060	0.25	4.2
18.0	0.11	0.50	4.6	7.0	0.08	0.300	3.7	2.0	0.050	0.20	4.0
10.0	0.08	0.30	3.7	5.0	0.06	0.200	3.3	1.0	0.025	0.07	2.8
3.0	0.05	0.18	3.6	3.0	0.05	0.150	3.0	0.5	0.030	0.045	1.5
1.0	0.04	0.08	2.0	0.1	0.009	0.200	2.2	0.4	0.040	0.05	1.2
0.4	0.04	0.06	1.5	0.01	0.007	0.009	1.3	0.1	0.070	0.10	1.4
0.003	0.003	0.004	1.3	0.01	0.007	0.008	1.1	0.08	0.060	0.07	1.6

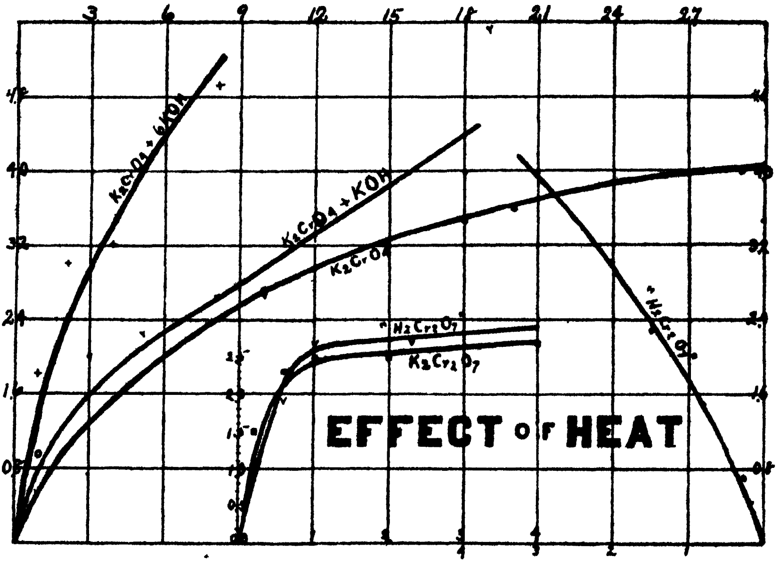

Plate III.

heated samples. The *ratios of color* (*r*) of the cold and heated samples are calculated from the two columns immediately preceding columns (*r*).

It is observed that an increase of about 80° of temperature: (1) intensifies[1] the color of all these solutions from one to six times; (2) concentrated solutions give the largest change of color. This latter effect is to be expected since *the mass-influence of water and the influence of heat are opposite.*

Preliminary experiments with picric acid, *o*-nitrophenol, their alkaline salts, both in cold and hot solutions, show variations of colors in varied concentrations, which indicate tautomeric changes, in accordance with the conclusions of Hantzsch. These substances will be studied by the methods of investigation of this contribution.

Solutions of chromates less concentrated than 0.001% are decolorized on long standing in direct sunlight. This phenomenon will also be investigated.

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[1] Hantzsch and Clark (*Z. physik. Chem.*, 63, 373) held that there is little or no effect of heat on chromate solutions as measured by light-absorption. Their data does not justify this conclusion.

Summary.

(1) Previous investigations have involved too limited a range of concentrations to elucidate the nature of chromate solutions.

(2) Hydrolytic equilibrium-changes involve color-changes; hydration-equilibria, though less important, also cause color-changes; ionization-equilibria, except as involving hydrolysis or hydration, probably have no effect on color-changes.

(3) Heat has marked effects on colors.

(4) Varied quantities of acids and alkalies have very important effects on the colors of chromates.

(5) Very dilute solutions of all chromates (CrO_3, H_2CrO_4, $H_2Cr_2O_7$, $H_2Cr_3O_{10}$, $H_2Cr_4O_{13}$) contain only chromate molecules or ions.

(6) More concentrated solutions contain both H_2CrO_4 and $H_2Cr_2O_7$ molecules and ions; chromate solutions contain dichromates and *vice versa*.

(7) At still greater concentrations or in acid solutions or when heated, dichromates contain trichromates and, probably at still greater concentrations, trichromates contain tetrachromates.

(8) Below the chromate-dichromate transition concentration, hydrated forms of chromate exist and probably produce color-variations.

SEATTLE, WASH

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE IDEAL DIFFUSION COEFFICIENT AND A FUNDAMENTAL LAW CONCERNING THE DIFFUSION OF DISSOLVED SUBSTANCES IN LIQUIDS.

BY GEORGE MCP SMITH.

Received March 13, 1914.

Introduction.

The significance of the diffusion coefficient D is derived from the formula,

$$dS = -Dq\frac{dc}{dx}dt,$$

in which dS is the quantity of the dissolved substance which passes at the point x in the time dt through the cross-section q of a diffusion cylinder under the influence of the concentration-fall dc/dx. The value of D depends upon the temperature and upon the actual concentration.

If we consider an ideal diffusion cylinder of unit cross-section, 1 cm.^{2}, in which the concentration difference 1 exists in the solution between two horizontal planes 1 centimeter apart, and in which the solution in the plane half-way between these has the concentration c, then the concentration of the solution in the lower plane is $c + {}^1/_2$, and that of the solution in the upper plane is $c - {}^1/_2$. The diffusion upwards, then, is caused by the existence of a concentration-fall of unity in the unit distance. If dc/dx in the above formula is equal to 1 gram per centimeter, then dS will be expressed in grams; or, if dc/dx is equal to 1 mol per centimeter, dS then will be expressed in mols. In both cases the numerical values of dS will be identical. A simple definition of D is as follows:

The diffusion coefficient D is the quantity of the dissolved substance, in grams, which passes in unit time, *e. g.*, 1 day, in the unit cross-section, 1 cm.^{2}, through the unit concentration-fall, 1 g., with unit velocity, 1 cm. per day.[1]

If, now, in a table of diffusion coefficients, determined at a given temperature with dilute solutions of substances which do not ionize or present other complications, we divide each D-value by the molecular weight of the substance in question, we obtain a set of *special* diffusion coefficients, D/M, which may be defined as the *number of mols* of the dissolved substance which in the unit cross-section pass in unit time through the *concentration-fall of one gram* with unit velocity.

Identical numerical values of D/M can, of course, be derived from the diffusion coefficients when dc in the above equation is expressed in terms of molal concentration. In that case, D is the number of mols of the dissolved substance that diffuse in unit time through unit area under the influence of a concentration-fall of one mol in unit distance; and, as has already been pointed out, the numerical values are identical with those of D as defined above.

But the question at once arises as to the physical significance of the values obtained by dividing these numbers, which are already expressed in mols, by the molecular weights of the respective compounds.

Here the values of D/M may be regarded as obtained in each case by dividing the weight of D mols of an ideal compound of unit molecular weight by the molecular weight of the respective compound.

The significance of the values thus obtained is as follows: If, *in each case*, the molecules of the ideal compound be regarded as possessing the same size and configuration and the same mean free-path velocity as those of the real compound, then they would encounter the same resistance that the latter do in their progressive forward movement; but the momentum of each such imaginary molecule of unit molecular weight would be equal only to the reciprocal value of that of a molecule of the real compound. That is to say, that only D/M mols of the imaginary substance would diffuse through unit distance in the time that it takes for D mols of the compound to do the same thing.

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[1] This is simply an expression in English of the value of dS in the above formula when $q = 1$ cm.^{2}, $dc = 1$ gram, $dx = 1$ cm., and $dt = 1$ day.

Viewed in this light, the values of D/M assume a real physical significance, *and we obtain in them a common denominator, the ideal diffusion coefficient,*[1] *to which the ordinary diffusion coefficients of different substances may be reduced,* provided that the molecules of the substances do not ionize or engage in other disturbing complications.

The IDEAL DIFFUSION COEFFICIENT, $D/M = I$, *indicates the number of mols of a compound which in the unit cross-section would pass in unit time through the unit molal concentration-interval with unit velocity, provided that each molecule of the compound—while retaining its size, configuration, and free-path velocity—had its momentum reduced to the reciprocal value.*

A. The Ideal Diffusion Coefficient and the Diffusion of Dissolved Substances in Water.

L. W. Öholm, who has carried on most of his work with aqueous solutions, has determined numerous diffusion coefficients at comparable temperatures and, in the case of almost every individual substance, at different concentrations; he has investigated the diffusion of many electrolytes,[2] and also that of many non-electrolytic organic compounds[3] with molecular weights varying all the way from 59 to 504. His results in the latter case are particularly valuable, since without them much necessary data would not be available at the present time.

TABLE I[4]

	Substance.	Equivalent concentration	Diffusion coefficient D	Molecular weight M.	Ideal diffusion coefficient 10^4. I	Log M	Log 10^4 I
1.	Acetamide ...	0.25	0.900	59	152.5	1.77085	2.18339
2	Urea... ...	0.25	1.022	60	170.3	1.77815	2.23130
3.	Dicyandiamide..	0.2	0.895	84	106.5	1.92428	2.02754
4.	Glycerol....	0.25	0.705	92	76.6	1.96379	1.88440
5.	Hydrochinone. .	0.25	0.665	110	60.5	2.04139	1.78143
6.	Resorcinol.....	0.25	0.652	110	59.3	2.04139	1.77286
7	Saligenin.......	0.25	0.619	124	49.9	2.09342	1.69827
8.	Penta-erythrite..	0.2	0.589	136	43.3	2.13354	1.63658
9.	Alloxan...... .	0.25	0.563	142	39.6	2.15229	1.59822
10.	Mannite........	0.25	0.485	182	26.6	2.26007	1.42567
11.	Ecgonine.......	0.1	0.604	185	32.6	2.26717	1.51387
12.	Caffeine...	0.05	0.488	194	25.2	2.28780	1.40062
13.	Salicin..........	0.12	0.402	286	14.1	2.45637	1.14786
14.	Cane sugar......	0.25	0.369	342	10.8	2.53403	1.03300
15.	Milk sugar......	0.2	0.361	342	10.6	2.53403	1.02348
16.	Raffinose..	0.25	0.297	504	5.9	2.70243	0.77033

---

[1] Owing to the importance of this new unit of diffusion, the writer would suggest the use of the capital letter I as its symbol.

[2] *Z. physik. Chem.*, **50**, 309–49 (1904–05).

[3] *Ibid.*, **70**, 378–407 (1910); *Chem. Zentr.*, **1913**, I, p. 1649 f.

[4] The D values in the table are taken from the work of L. W. Öholm, *Z. physik. Chem.*, **70**, 401 (1910), and *Chem. Zentr.*, **1913**, I, p. 1649. In this table water of crystallization was not taken into consideration.

If now, in the cases of substances of varying molecular weights, such as those listed in Table I, we plot the values of the ideal diffusion coefficients as ordinates and those of the molecular weights as abscissas, we obtain the curve shown in Fig. 1.

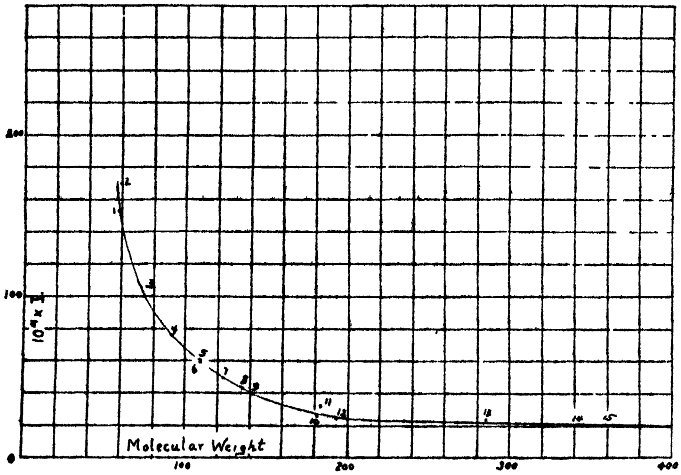

Figure 1

From the appearance of this curve it occurred to the writer also to plot the logarithms of these values, and upon doing so the straight line *BC* shown in Fig. 2 was obtained.

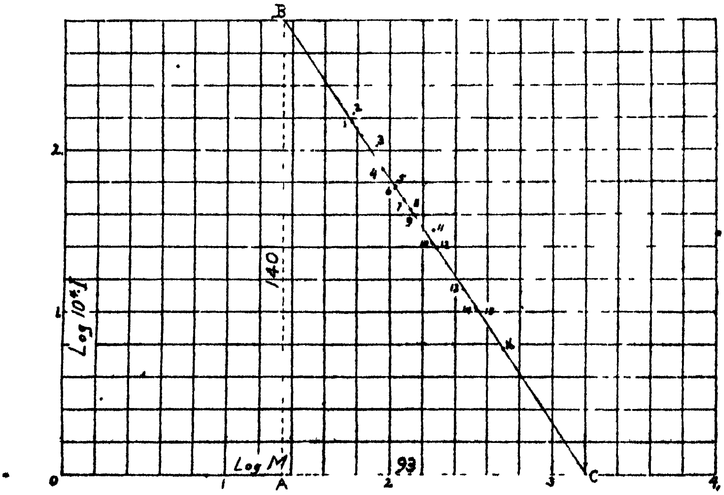

Figure 2

As the graph of the straight line *BC*, in Fig. 2, we have the equation:

$$\log \mathrm{I} + n \log M = \log K,$$

TABLE II[1]

	Substance	c	$D_{20°}$.	M	Log M	$10^4 \times I$	Log I	Log IM^n.	K
1.	Acetamide	0.25	0.900	59	1.77085	152.5	—2.18339	0.84922	*7.07*
2	Urea	0.25	1.022	60	1.77815	170.3	—2.23130	0.90812	8.09
3.	Dicyandiamide	0.2	0.895	84	1.92428	106.5	—2.02754	0.92435	8.40
4.	Glycerol	0.25	0.705	92	1.96379	76.6	—3.88440	0.84068	*6.93*
5.	Hydrochinone	0.25	0.665	110	2.04139	60.5	—3.78143	0.85453	*7.15*
6.	Resorcinol	0.25	0.652	110	2.04139	59.3	—3.77286	0.84596	*7.02*
7	Saligenin	0.25	0.619	124	2.09342	49.9	—3.69827	0.84970	*7.07*
8.	Penta-erythrite	0.2	0.589	136	2.13354	43.3	—3.63658	0.84841	*7.05*
9.	Arabinose	0.25	0.552	150	2.17609	36.8	—3.56585	0.84173	*6.95*
10.	Nicotine	0.1	0.456	162	2.20952	28.1	—3.44944	0.77565	5.97
11.	Mannite	0.25	0.485	182	2.26007	26.6	—3.42567	0.82797	6.73
12.	Ecgonine	0.1	0.604	185	2.26717	32.6	—3.51387	0.92686	8.45
13.	Alloxan (4 H_2O)	0.25	0.563	214	2.33041	26.3	—3.42010	0.92829	8.48
	Alloxan (anhydrous)	0.25	0.563	142	2.15229	39.6	—2.59822	0.83827	*6.89*
14.	Caffeine (1 H_2O)	0.05	0.488	230	2.36173	21.2	—3.32669	0.88203	7.62
	Caffeine (anhydrous)	0.05	0.488	212	2.32634	23.0	—3.36208	0.86415	7.31
15.	Salicin	0.12	0.402	286	2.45637	14.1	—3.14786	0.84567	*7.01*
16.	Cane sugar	0.25	0.369	342	2.53403	10.8	—3.03300	0.84772	*7.04*
17.	Maltose (1 H_2O)	0.25	0.348	360	2.55630	9.67	—4.98528	0.83353	*6.82*
	Maltose (anhydrous)	0.25	0.348	342	2.53403	10.2	—3.00755	0.82227	6.64
18.	Milk sugar (1 H_2O)	0.2	0.361	360	2.55630	10.0	—3.00121	0.84946	*7.07*
	Milk sugar (anhydrous)	0.2	0.361	342	2.53403	10.8	—3.02348	0.83820	6.89
19.	Raffinose (5 H_2O)	0.25	0.297	594	2.77379	5.00	—4.69895	0.87461	7.49
	Raffinose (anhydrous)	0.25	0.297	504	2.70243	5.89	—4.77033	0.83856	*6.90*

Mean of the 13 values in italics = 7.00

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[1] In the case of compounds containing water of crystallization, two values of K are calculated; the values of D expressed in mols are the same in either case.

in which K is a constant and n is the slope of the line BC. *From this there is obtained a new fundamental law of diffusion, which is expressed by the formula,*

$$I M^n = K,$$

from which, if the values of n and K have been determined for a given set of conditions, the corresponding value of I in the case of any substance of known molecular weight, and therefore the theoretical value of D, may be calculated; or, if, in the case of a given substance, the value of D has been determined experimentally, then the molecular weight of the substance may be calculated. We have the formulae:

$$I = K/M^n; \quad D = IM; \quad M = (K/D)^{1/n-1}.$$

In the case of the hydrodiffusion of non-electrolytes in dilute solution at 20°, we obtain from Fig. 2 for the slope of the line BC the value,

$$n = AB/AC = 140/93 = 1.5054.$$

The values of K for this case are given in Table II.

In his first paper on the hydrodiffusion of the non-electrolytes, Öholm[1] plots the values of D at 20° for different concentrations, and, by continuing the curves to the Y-axis, he obtains the values at infinite dilution; from these values of D he derives four of the values of $D\sqrt{M}$ given in Table III. His values for M, however, are those of the compound without its water of crystallization, and to the writer it would appear unjustifiable to leave this entirely out of consideration. For that reason three more values have been added in italics.

The approximate relation, $D\sqrt{M}$ = const., has been derived[2] from Graham's law for the *effusion* of gases through narrow openings in thin solid partitions; the law does not hold strictly, even in the case of gases, for *diffusion*.

TABLE III.[3]

	A.			B.				
	D_∞ 20°.	$\sqrt{M}$.	$D\sqrt{M}$.	t°.	c.	D.	M.	$D\sqrt{M}$.
Cane sugar........	0 382	18.5	7.067	11 0	0.25	0 282	342	5.2
Milk sugar...........	0.377	18.5	6.975	.	.	...	. .	...
Milk sugar + H_2O...	*0 377*	*18.97*	*7.151*	....	..		..	.
Maltose..............	0.373	18.5	6.901	10.2	0 25	0.280	342	5.2
Maltose +. H_2O.......	*0.373*	*18.97*	*7.076*	*10.2*	*0.25*	*0.280*	360	*5.3*
Raffinose.............	0.316	22.45	7.096	10.8	0.25	0 230	504	5.2
Raffinose + $5H_2O$.....	*0.316*	*24.37*	*7.701*	*10.8*	*0.25*	*0.230*	594	*5.6*

Öholm[4] has determined the values of D_∞ at 20° for dextrin, arabinose, and nicotine, in addition to those for the four sugars listed in Table III. He also has determined the corresponding values in the cases of the substances investigated in his second paper, but, since his values are not included in the abstract of his paper,[1] they have been redetermined by the writer according to Öholm's method. The method is shown in Fig. 3,

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[1] *Z. physik. Chem.*, 70, 400–404.

[2] Cf. F. Exner, *Pogg. Ann.*, 155, 457 f (1875); G. Hüfner, *Wied. Ann.*, 60, 134 (1896); H. Euler, *Ibid.*, 63, 273 (1897).

[3] Öholm does not calculate the values of $D\sqrt{M}$ for the diffusion data at 10°; these are given, however, under B of this table.

[4] *Z. physik. Chem.*, 70, 400 f.

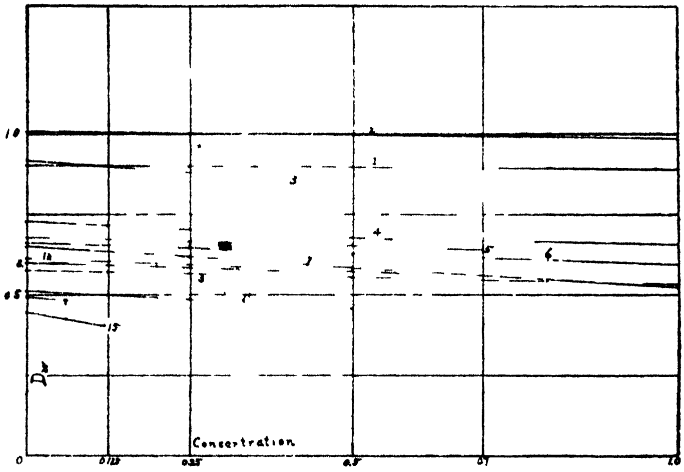

Figure 3

and the numerical results are given in Table IV, together with Öholm's values for the seven substances referred to above

The values of log M and of log $10^4 I$ in Table IV are plotted in Fig. 4[1] and from these we get the relation,

$$n = AB/AC = 140/94 = 1.4894.$$

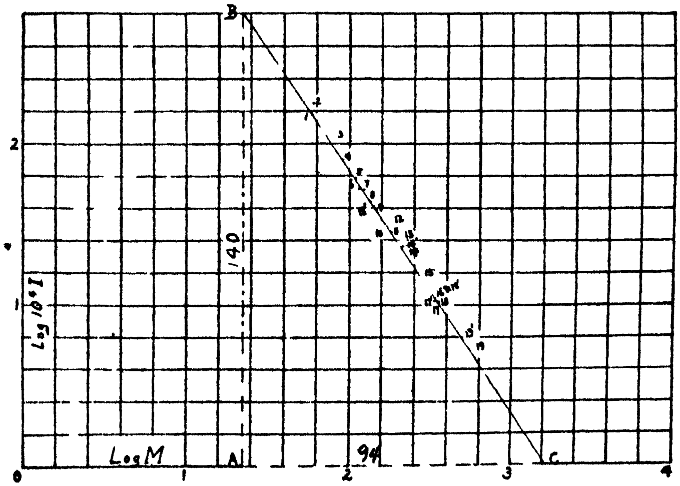

Figure 4

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[1] *Chem. Zentr.*, 1913, I, 1649.

TABLE IV.[1]—DIFFUSION DATA AT 20° FOR INFINITE DILUTION.

	Substance.	D_∞.	*M*.	Log *M*.	$10^4 \times I$.	Log *I*.	Log IM^n.	*K*.
1.	Acetamide	0.902	59	1.77085	152.9	—2.18436	0.82184	*6.64*
2.	Urea	1.070	60	1.77815	178.3	—2.25123	0.89960	[7.93]
3.	Dicyandiamide	0.920	84	1.92428	109.5	—2.03951	0.90551	[8.04]
4.	Glycerol	0.730	92	1.96379	79.3	—3.89953	0.82438	*6.67*
5.	Hydrochinone	0.678	110	2.04139	61.6	—3.78984	0.83027	*6.76*
6.	Resorcinol	0.660	110	2.04139	60.0	—3.77815	0.81858	*6.59*
7.	Saligenin	0.650	124	2.09342	52.4	—3.71949	0.83741	*6.88*
8.	Penta-erythrite	0.600	136	2.13354	44.1	—3.64461	0.82229	*6.64*
9.	Arabinose	0.582	150	2.17609	38.8	—3.58883	0.82988	*6.76*
10.	Nicotine	0.476	162	2.20952	29.4	—3.46809	0.75893	[5.74]
11.	Mannite	0.511	182	2.26007	28.1	—3.44835	0.81448	*6.52*
12.	Ecgonine	0.612	185	2.26717	33.1	—3.51958	0.89628	[7.87]
13.	Alloxan (4 H_2O)	0.575	214	2.33041	26.9	—3.42926	0.90016	7.95
13′.	Alloxan (anhydrous)	0.575	*142*	2.15229	*40.5*	—3.60738	0.81299	*6.50*
14.	Caffeine (1 H_2O)	0.490	230	2.36173	21.3	—3.32847	0.84611	[7.01]
14′.	Caffeine (anhydrous)	0.490	*212*	2.32634	*23.1*	—3.36386	0.83870	[6.90]
15.	Salicin	0.445	286	2.45637	15.6	—3.19199	0.85048	[7.25]
16.	Cane sugar	0.382	342	2.53403	11.2	—3.04803	0.82220	*6.64*
17.	Maltose (1 H_2O)	0.373	360	2.55630	10.4	—3.01541	0.82275	*6.65*
17′.	Maltose (anhydrous)	0.373	*342*	2.53403	*10.9*	—3.03768	0.81185	6.48
18.	Milk sugar (1 H_2O)	0.377	360	2.55630	10.5	—3.02004	0.82738	*6.72*
18′.	Milk sugar (anhydrous)	0.377	*342*	2.53403	*11.0*	—3.04231	0.81648	6.55
19.	Raffinose (5 H_2O)	0.316	594	2.77379	5.32	—4.72590	0.75716	5.72
19′.	Raffinose (anhydrous)	0.316	*504*	2.70243	*6.27*	—4.79726	0.82225	*6.64*
20.	Dextrin	0.103	172*x*					

Mean of the 13 values in italics. $K = 6.66$

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[1] The numbers in Fig. 3 correspond to those of the compounds listed in this table. $n = 1.4894$.

Making use of the empirical formula, $D_\infty \times \sqrt{M} = 7$, at 20°, Öholm[1] obtains for the molecular weight of dextrin the numerical value 4440, from which x in the formula $(C_6H_{10}O_5)_x$ assumes the value 27.3.

Upon employing the formula given above, we obtain for M the value,

$$M = (K/D)^{1/n-1} = (6.66/0.105)^{2.0433} = 4815;$$

and for x the value,

$$x = 4815/162 = 29.72.$$

Öholm[2] assigns to dextrin the formula $(C_6H_{10}O_5)_{27\pm1}$; in the light of the above calculation, the formula would be $(C_6H_{10}O_5)_{30}$, of which the theoretical molecular weight is 4860.

Upon comparing the data in Tables II and IV, it will be seen that in each table there are six substances that behave abnormally. Five of these are common to both tables, namely urea, dicyandiamide, nicotine, ecgonine, and caffeine.[3] Salicin,[3] which is normal in Table II, behaves abnormally in Table IV; and mannite does the opposite, though it is almost normal in Table II.

Of the substances that are known with water of crystallization, caffeine is abnormal. But in both tables maltose and milk sugar give values of K which are closer to the mean if we derive the value of M from the hydrated compounds. On the other hand, alloxan and raffinose, which crystallize with 4 and 5 molecules of water, respectively, give normal values of K only if we derive the value of M from the anhydrous compounds. The behavior of these substances would seem to depend upon the relative stability of their hydrates at 20°; the explanation may lie in the existence of an equilibrium between the hydrate on the one hand and the anhydrous compound and water on the other.

By plotting the logarithms of M and I, in the case of Öholm's data[4] at about 10°, the value of n in the formula $IM^n = K$ was found to be 1.4286 for 0.25 molal solutions. Then by substituting this value for n in the formula $M = (K/D)^{(1/n-1)}$, the value of K (= 3.354) having been determined by calculation for anhydrous raffinose, the molecular weights of the other substances have been calculated. The results are given in Table V.

TABLE V.

	$t°$.	c.	D.	K.	$(K/D)^{1/n-1}$.	Theoretical value M.
Arabinose	9.4	0.25	0.388	.	153	150
Cane sugar	11.0	0.25	0.282	...	323	342
Maltose (1 H_2O)	10.0	0.25	0.272	...	351	360
Raffinose	10.9	0.25	0.233	3.354	...	...

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[1] *Z. physik. Chem.*, 70, 404 f.

[2] *Ibid.*, p. 405.

[3] A possible explanation for the abnormal behavior of caffeine, and of salicin in this case, is offered in a footnote on p. 858.

[4] *Z. physik. Chem.*, 70, p. 393 ff.

B. The Ideal Diffusion Coefficient and the Diffusion of Gases through Water.

According to the well-known law of Graham, the *effusion* velocities of two gases vary inversely as the square roots of their densities. This law was later extended by Exner[1] also to the passage of gases through absorbent liquids, and according to him the volumes of two gases that pass through the liquid film in a given time roughly vary directly as their absorption coefficients and inversely as the square roots of their densities.

Exner studied the passage of gases through very thin soap-bubble membranes only; but later, G. Hüfner[2] studied the phenomenon in the case of thicker layers of liquid. He succeeded in overcoming the difficulties which arose from convection currents in the thicker layers by placing the water upon a thin plate of *hydrophane*—a porous mineral which absorbs water, but through which water does not pass except under appreciable pressure—and allowing the diffusing gas to enter from below or above as the case might require.

The process just referred to differs essentially from effusion and from diffusion in the narrower sense in that the water of the partition is capable of absorbing the gases, so that it takes the gas in at one side and gives it out at the other. It is conditioned, not only by the state of motion of the gaseous substance but also by the movements of the molecules of the liquid partition; and especially by the fact that the gaseous molecules have to penetrate the surface film of the liquid, both upon entering and upon leaving the latter.

In Hüfner's experiments with oxygen, for example, the lower part of the vertically disposed diffusion tube contained moist oxygen; above this there was situated the hydrophane plate, covered with a column of water 1 or 2 cm. high and about 0.75 cm. in diameter, through which the gas was allowed to diffuse upwards. The upper surface of the water was kept in contact with fresh nitrogen gas, which, saturated with moisture, was very slowly passed through this part of the diffusion tube.[3]

In slowly diffusing upwards through the column of water, under these conditions, the oxygen gas is supposed to keep the lowest layer of the water saturated with itself; the uppermost layer of the water, however, always contains only a relatively insignificant quantity of dissolved oxygen, since by means of the current of nitrogen the partial pressure of the former gas above the surface of the water is kept practically at zero.

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[1] *Pogg. Ann.*, 155, 321, 443 (1875).

[2] *Wied. Ann.*, 60, 134–68 (1896); *Z. physik. Chem.*, 27, 227–49 (1898).

[3] For detailed particulars in regard to the experimental work, the reader is referred to the original papers of Hüfner. It may be stated, however, that allowance was made in the calculation for the resistance of the hydrophane plate; *e. g.*, in the case of carbon dioxide, 0.4202 cc. (calc. for 760 mm.) passed through the plate and a 0.5 cm. layer of water in 1 day at 16.4°, and 0.2105 cc. passed through the plate and a 2.0 cm. layer of water in the same time at 16.3°. Then, assuming that the diffusing gas-volumes vary inversely as the thickness of the (water) layers penetrated, $0.4202\ (w + 0.5) = 0.2105\ (w + 2.0)$, whence $w = 1.005$ cm.; *i. e.*, in order to pass through the moist hydrophane plate 0.05 cm. thick, carbon dioxide requires the same time as it would under like conditions require to pass through a layer of water with the same cross-section but 1.005 cm. thick

Now, if the water column were 1 cm. thick and its cross-sectional area equal to 1 cm^2., and if the partial pressure of the oxygen gas below it were kept equal to 1 atm., then in the lowest layer of the liquid there would be maintained a concentration of dissolved oxygen equal to α cc. of the gas per cc. of solution, α being the absorption coefficient of oxygen for water at the temperature of the experiment *e. g.*, 0.030 at 21.7°. That is to say, the concentration difference between the top and bottom layers of the liquid would be equal to 0 030 cc.; and if, under these conditions, 0.048535 cc. of oxygen diffused through the column of water in 1 day, then 0.048535 ÷ 0.030 = 1.62 cc.[1] would have diffused through in the same time, had the concentration difference between the two layers been kept equal to 1 cc., or 1.62 mols would have done the same had the concentration difference been maintained at 1 mol per cm. In other words, 1.62 is the diffusion coefficient of oxygen *through* water, at 21.7°.

As a matter of fact, it is possible that the lowest layer of the liquid is never completely saturated with the gas, under the above conditions, and it is difficult to believe that the concentration of the dissolved gas in the uppermost layer of the water is equal to zero. This assumption presupposes that the dissolved gas molecules are able to leave the upper layer of the water without encountering any more resistance than they meet in their upward passage through the liquid; while in reality they do have to break through the dense surface film of the water in order to escape into the gaseous space above. In this respect the values of the diffusion coefficients of gases *through* water, as determined by Hüfner, would seem to be not strictly comparable with the values obtained for the diffusion of dissolved substances *in* water; they are, however, certainly comparable among themselves.

The experimental results of Hüfner are given in Table VI, and in Fig. 5 are plotted the logarithms of the ideal diffusion coefficients and those of the molecular weights of the gases. The corresponding values at infinite dilution for acetamide, one of the substances of normal behavior in Table IV, are also plotted, in order to show what position the curve in Fig. 4 would assume in relation to that for the gases now being considered. The value of n in this case is,

$$n = 140/192 = 1.5326.$$

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[1] Hüfner himself designates this as 1.62 cm., evidently meaning that 1 cc. of the gas would pass through 1 62 cm. of water per cm^2 of surface, under a concentration difference of 1 cc. per cm. distance.

TABLE VI.[1]

	Gas.	t°.	D.	$D\sqrt{M}$.	$I \times 10^3$.	Log M.	Log $10^3 I$.	$IM^n = K$.
1.	Hydrogen......	16.	7.53	10.6	376.5	0.30103	2.57576	10.8
2.	Hydrogen......	21.	4.45	...	222.5	0.30103	2.34733	...
3.	Hydrogen......	16.	4.09	...	204.5	0.30103	2.31069	...
4.	Ammonia......	20.0	1.260	5.2	7.41	1.23045	0.86992	5.5
5.	Nitrogen.......	21.7	1.73	9.2	6.17	1.44747	0.79058	9.8
6.	Oxygen.......	21.7	1.62	9.2	5.06	1.50515	0.70437	9.9
7.	Nitrous oxide..	16.2	1.35	9.0	3.07	1.64365	0.48668	9.7
8.	Carbon dioxide.	16.4	1.37	9.1	3.11	1.64345	0.49327	9.9
9.	Chlorine..... ..	16 3	1.098	9.3	1 55	1.85077	0.18983	10.1
10.	*Acetamide......*	*20.0*	*0.902*	*(6.93)*	*1.529*	*1.77085*	*0 18436*	*(6.64)*

When we consider the experimental difficulties encountered by Hüfner in determining such small quantities of gas as those which actually diffused through the water in his apparatus, the appearance of the curve in Fig. 5 is striking, to say the least; it is very near, and practically parallel to that obtained in Fig. 4, and, in spite of the probable justness of the considerations advanced on p. 857, together with the effect of the counter diffusion of another gas, the gases nevertheless appear to diffuse faster than the theory would require. The cause of this may partially lie in the extremely low concentration of the solutions with which the experiments in the case of the gases were actually performed.[2]

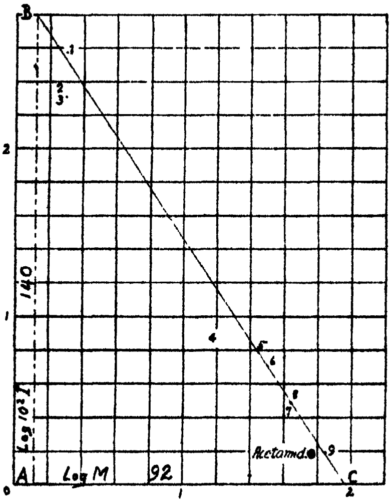

Figure 5.

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[1] Hüfner obtained the first value for hydrogen by means of the capillary method of Stefan; the gas entered, but did not leave the water. Hüfner himself does not consider the value exact. The second and third values were obtained by the hydrophane method, the former with the counter diffusion of air, the latter with that of carbon dioxide. This fact, together with the difference in temperature, might well account for the different figures. However, the absorption coefficient of hydrogen for water is so small that the latter values are probably farther removed from the truth than the first.

The value for ammonia was obtained by the diffusion of ammonia gas into water in a diffusion cylinder so arranged that the gas entered from above, while fresh running water was kept in contact with the lower surface of the hydrophane plate, the vertical arm of the diffusion tube which held the plate being immersed in the water.

The value for chlorine was obtained by means of Stefan's capillary method.

[2] The molal concentration of saturated solutions of the gases at the temperatures of the experiments and at 760 mm. have maximum values as follows: H_2 = 0.0008, N_2 = 0.0007, O_2 ± 0.0014, N_2O = 0.033, CO_2 = 0.043, and Cl_2 = 0.11. It will be noted in Fig. 3 that D for caffeine, which diffused too fast, was actually determined

It will be noted in the table that the values for ammonia are very abnormal; Hüfner[1] was unable to account for this in a satisfactory manner. He does mention that Scheffer[2] found for ammonia at 4.5° a diffusion coefficient of 1.06—a higher value than he himself found at 13° (1.052). The reason for this is really not far to seek; the absorption coefficient of ammonia is 760 at 13°, *i. e.*, 1 cc. of water at this temperature will dissolve 0.57 gram of ammonia gas, giving about 1.75 cc. of solution. Such a solution is nearly 20 times normal! Neither were Scheffer's solutions dilute; they were about 0.6 and 3.0 normal, respectively.[3]

C. The Ideal Diffusion Coefficient and the Diffusion of Metals in Mercury.

M. von Wogau[4] has carried out an extensive investigation on the diffusion of metals in mercury, and it was in this connection that the writer, some years ago, published a paper,[5] of which the present one may be regarded as a continuation.

Although at that time it had been shown that the crystalline amalgams of the alkali and alkali earth metals are chemical compounds of the respective metals with mercury, von Wogau, in the discussion of his experimental results, assumed that these metals existed in mercurial solution in the form of monatomic molecules. It has since been shown by the writer[6] that even in dilute mercurial solution the metals in question exist in the form of compounds of the general formula $MeHg_n$, containing only one atom of the alkali or alkali earth metal to the molecule. And, taking the mass law into consideration, it would indeed be a surprising fact if the compounds in question did dissociate to a marked degree upon the addition of a large excess of mercury.[7]

If, however, granting for the time being the assumption of von Wogau, we plot the logarithms of the resulting ideal diffusion coefficients of the metals listed in Table VII with those of their molecular (*i. e.*, atomic) weights, we obtain the points shown in Fig. 6.

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only at 0.05 molal concentration. Also salicin, which in Table II, at 0.12 molal concentration, has normal values, was also determined at 0.07 molal concentration, and the value at infinite dilution obtained from these values gave to it an abnormal value. No other substances in Table IV were measured at concentrations below 0.1 molal.

[1] *Z. physik. Chem.*, **27**, 236

[2] *Ibid.*, **2**, 390 (1888).

[3] Cf. note to Table VI.

[4] *Ann. Physik*, [4] **23**, 345–70 (1907).

[5] *Ibid.*, [4] **25**, 252 (1908); *Z. anorg. Chem.*, **58**, 381 (1908).

[6] *Z. anorg. Chem.*, **58**, 381 (1908). A summary of the literature concerning the crystalline compounds may be found in this paper.

[7] Heycock and Neville, *J. Chem. Soc.*, **55**, 671 (1889), actually do suppose that a compound is formed upon the addition of sodium to mercury, which, upon the further addition of sodium, dissociates into sodium and monatomic mercury molecules.

TABLE VII.

	Amalgam.	Number of separate determinations.	Average temperature. $t°$.	Average concentration. %.	Mean value. D.	Exner's rule. $D\sqrt{A}$.	Atomic weight. M.	Log M.	Log $10^3 I$.
1.	Lithium......	3	8.2	0.141	0.66	1.75	6.94	0.84136	1.97818
2.	Sodium.....	4	9.6	0.140	0.64	3.07	23.00	1.36173	1.44445
3.	Potassium....	5	10.5	0.119	0.53	3.32	39.10	1.59218	1.13210
4.	Calcium....	2	10.2	0.1	0.54	3.42	40.07	1.60282	1.12957
5.	Zinc.........	6	11.5	0.1033	2.18	17.63	65.37	1.81538	1.52308
5′.	Zinc.........	3	*99.2*	0.112	*2.90*	*23.5*	65.37	1.81538	1.64702
6.	Rubidium...	3	7.3	0.157	0.46	4.25	85.45	1.93171	0.73105
7.	Strontium....	5	9.4	0.144	0.47	4.40	87.63	1.94265	0.72955
8.	Cadmium....	3	8.7	0.128	1.45	15.37	112.40	2.05077	1.11060
8′.	Cadmium....	3	*99.1*	0.130	*2.96*	*31.4*	112.40	2.05077	1.42052
9.	Tin..........	4	10.7	0.145	1.53	16 7	119.0	2.07555	1.10914
10.	Caesium....	4	7.3	0.1475	0.45	5.19	132.81	2.12323	0.52998
11.	Barium....	3	7.8	0.093	0.52	6.10	137.37	2.13789	0 57811
12.	Thallium.....	4	11.5	0.144	0.87	12.43	204.0	2.30963	0.62989
13.	Lead........	3	9.4	0.138	1.50	21.6	207.1	2.31618	0.85991
13′.	Lead........	2	*99.2*	0.138	*1.92*	*27.6*	207.1	2.31618	0.96712

In this case also von Wogau tests Exner's rule that $D\sqrt{M}$ = const., assuming as the values of M the atomic weights of the respective metals. He finds the values that are listed in Table VII under the heading $D\sqrt{A}$, and which are far from being constant.

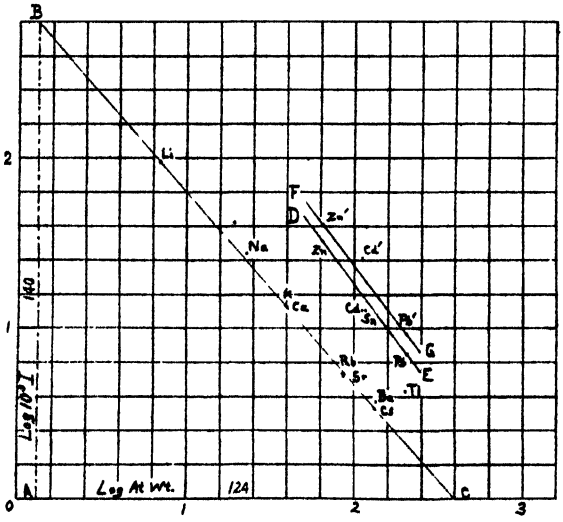

Figure 6.

Long before this, Ostwald[1] had expressed the view that—in harmony with the relationship, $D\sqrt{M}$ = const., as established by Hüfner[2] and Euler[2] for the diffusion of non-electrolytes in aqueous solution — the analogous relationship would be found to obtain for the diffusion of metals in mercurial solution; namely, that $D\sqrt{A}$ = const. G. Meyer,[3] on the other hand, pointed out that this was improbable, since the mean free-path l of the metallic atoms is proportional to the product $D\sqrt{A}$; and, if the latter were constant, then the atoms of all metals would have equal mean free-paths.[1]

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[1] *Z. physik. Chem.*, **24**, 530 (1897)

[2] *Loc. cit.*

[3] *Wied. Ann.*, **64**, 752 (1898).

Turning now to Fig. 6, we note that the alkali and alkali earth metals all give values that fall on, or very near to, the line *BC*, while zinc and lead, which are known to be incapable of combination with mercury,[2] at about 10° fall on the line *DE*, and at 99° on the line *FG*, which is parallel to *DE*.

Thallium, which with mercury forms the compound $TlHg_2$,[3] gives a value that lies between the lines *BC* and *DE*; and as to cadmium and tin, which fall near the line *DE*, both Bijl[2] and Puschin,[2] and also Würschmidt,[4] conclude from their work that these metals are incapable of entering into combination with mercury. Van Heterin,[5] on the other hand, believes that he has found indications that tin may combine with mercury; he could not, however, derive a formula for the supposed compound.

TABLE VIII.[6]

	Dissolved substance	Average concentration. Mols per liter.	D	$D\sqrt{M}$.	M	Log M.	Log l	$lM^{\frac{1}{2}} = K$.
1.	Zn	0.214	2.18	17.6	65.37	1.81538	—2.52308	14.8
2.	Cd	0.154	1.45	15.4	112.4	2.05077	—2.11060	12.6
3	Sn	0.165	1.53	16.7	119.0	2.07555	—2.10914	13.7
4.	Pb	0.0902	1.50	21.6	207.1	2.31618	—3.85991	17.3
5.	$AuHg_2$	.	0.72	17.6	598.4	2.77699	—3.08034	13.5
6.	$TlHg_2$	0.0322	0.87	21.4	605.2	2.78190	—3.15762	16.1
7.	$LiHg_3$	0.0314	0.66	16.3	608.7	2.78440	—3.03514	12.5
8.	$NaHg_5$	0.0185	0.64	20.5	1026.	3.01115	—4.79503	16.4
9.	$CaHg_5$	0.0130	0.54	17.4	1043.	3.01828	—4.71411	13.0
10.	KHg_6	0.0130	0.53	18.7	1243	3.09447	—4.62981	13.9
11.	$RbHg_6$	0.0165	0.46	16.5	1289.	3.11025	—4.55251	12.3
12.	$SrHg_6$	0.0151	0.47	16.9	1291.	3.11093	—4.56117	12.5
13.	$CsHg_6$	0.0149	0.45	16.4	1336	3.12581	—4.52750	12.2
14.	$BaHg_6$	0.0094	0.52	19.0	1341	3.12743	—4.58857	14.1

Mean value: $K = 13.9$

By taking as a basis what is known in regard to the compounds formed by mercury with other metals, the writer has succeeded in arriving at the data given in Table VIII.[1] It will be noted that Exner's rule, that $D\sqrt{M} =$ const., roughly holds also in this case.

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[1] Riecke's molecular diffusion theory (*Z. physik. Chem.*, **6**, 504 (1890)) furnishes the formula: $l = 0.01332 \times 10^{-8} \times \sqrt{1 + 0.00367t} \times D\sqrt{M}$.

[2] H. C. Bijl, *Z. physik. Chem.*, **41**, 641 (1902); N. Puschin, *Z. anorg. Chem.*, **36**, 201–254 (1903); J. Würschmidt, *J. Chem. Soc.*, **104**, II, 101.

[3] N. S. Kurnakow and N. Puschin, *Z. anorg. Chem.*, **30**, 86 (1902).

[4] *Loc. cit.*

[5] *Z. anorg. Chem.*, **42**, 129 (1904).

[6] The value for gold, D = 0.72, at 11°, was determined by Roberts-Austen, *Proc. Royal Soc.*, **59**, 283 (1896).

The average molal concentrations of the amalgams were obtained on the assumption that the specific gravity of the dilute amalgams at about 10° is equal to that of mercury at 20° (*i. e.*, 1 liter = 13.546 kg.); this assumption is not far from the truth.

Plotting, now, the values of log M and of log $10^4 I$, we obtain the points shown in Fig. 7. They all lie on, or very near to, the line BC, and lead, which is known to be incapable of combining with mercury, occupies the position that is farthest removed from the line. For n we obtain in this case the value

$$n = AB/AC = 140/96 = 1.4583.$$

Substituting the value of n in the equation $IM^n = K$, we arrive at the values of K which are given in the last column of the table. The mean value derived from these is $K = 13.9$.

Assuming now that 13.9 is the correct value of K, the theoretical values of D can be calculated by means of the formula

$$D = K/M^{(n-1)} = 13.9/M^{0.4583}$$

These values are given in Table IX, together with those actually obtained by von Wogau.

TABLE IX[2]

	Dissolved substance.	Mean experimental value with probable error assigned by von Wogau.	Calculated D-value	Nearest result from a single experiment	Difference
1.	Zn	2.18 ± 0.16	2.047	2.04	−0.007
2.	Cd	1.45 ± 0.09	1.596	1.53	−0.066
3	Sn	1.53 ± 0.064	1.555	1.50	−0.055
4.	Pb	1.50 ± 0.09	1.207	1.48	+0.273
5	$AuHg_2$	0.72 (Roberts-Austen)	0.744		
6.	$TlHg_2$	0.87 ± 0.076	0.738	0.81	+0.072
7	$LiHg_3$	0.66 ± 0.045	0.736	0.72	−0.016
8.	$NaHg_5$	0.64 ± 0.017	0.579	0.63	+0.051
9.	$CaHg_6$	0.54 ± 0.022	0.575	0.56	−0.015
10.	KHg_6	0.53 ± 0.032	0.526	0.51	−0.016
11.	$RbHg_6$	0.46 ± 0.007	0.522	0.46	−0.062
12.	$SrHg_6$	0.47 ± 0.035	0.521	0.53	+0.009
13.	$CsHg_6$	0.45 ± 0.017	0.513	0.47	−0.043
14.	$BaHg_6$	0.52 ± 0.014	0.513	0.52	+0.007

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[1] Concerning the constitution of the liquid amalgams of the alkali and alkali earth metals, see G. McP. Smith, *Z. anorg. Chem.*, **58**, 381 (1908); and, in regard to the compounds $LiHg_3$ and $NaHg_5$ at ordinary temperatures, see G. McP. Smith and H. C. Bennett, THIS JOURNAL, **32**, 622 (1910), and *Z. anorg. Chem.*, **74**, 172 (1911).

[2] Gold being heavier than mercury was caused by Roberts-Austen to diffuse upwards. But, since all the other metals are specifically lighter than mercury (Pb = 11.3, Tl = 11.8), von Wogau was forced to measure their diffusion downwards. Accordingly, by means of a very ingenious arrangement of horizontally sliding plate-glass plates, each of which contained a single circular perforation, he gently slid the small disc of the amalgam (which filled the perforation of the upper plate) over the column of mercury which was contained in the concentric perforations of the lower plates. At the end of the experiment he separated the different sections of the mercurial solution by the same means, for analysis.

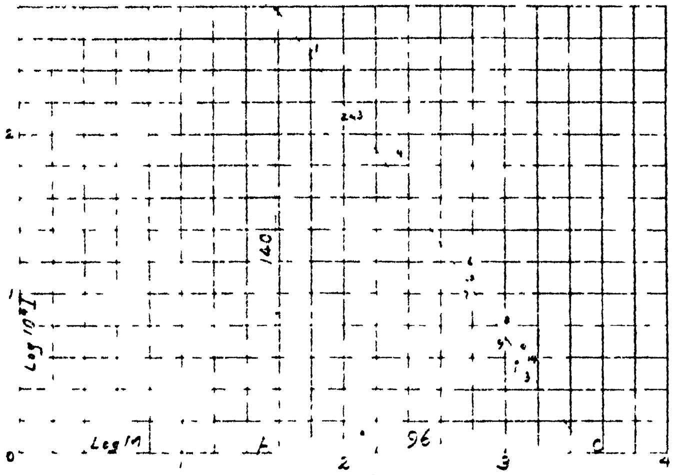

Figure 7.

The calculated values agree, on the whole, very well with those obtained by experiment.

D. The Equation $IM^n = K$, and Its Analogy to the Equation, pv^ν = const., for the Polytropic Expansion of Gases.

The values of n in the equation $IM^n = K$, in the cases discussed above, are given in Table X.

TABLE X.

Table.	Case	Concentration.	Temperature	n.
2.	Hydrodiffusion of organic compounds..	0.25	20°	1.5054
4.	Hydrodiffusion of organic compounds..	Infinitely dilute	20°	1.4894
5.	Hydrodiffusion of organic compounds	0.25	10°	1.4286
6.	Hydrodiffusion of gases	Very dilute	16°–20°	1.5326
8.	Diffusion in mercurial solution	Very dilute	About 10°	1.4583

It is now easy to explain Exner's rule, that $D\sqrt{M}$ = const., in terms of the above equation. Since in that equation $I = D/M$, we have,

$$IM^n = DM^{(n-1)} = K;$$

it will be seen in the table that in every case the value of $(n - 1)$ roughly approximates 0.5, whence we arrive at the rough approximation,

$$D\sqrt{M} = \text{const.}$$

The equation $IM^n = K$, which was derived in this form simply to facilitate the processes of calculation, may of course be converted into the form

$$MI^\nu = C,$$

in which $\nu = 1/n$ and C is a constant. In this form, the analogy that exists between this equation and that for the polytropic expansion of a gas—pv^ν = const.—will readily be recognized. Both equations are those of processes, and, in deriving the equation $MI^{\nu} = C$, we have analyzed the process of diffusion, which itself is one of expansion, into two components: one of these, I, corresponds to v, and the other, M, to p, in the equation $pv^{\nu} = \text{const.}$

In conclusion, it may be stated that, upon applying the ideas involved in the conception of the ideal diffusion coefficient to the hydrodiffusion of electrolytes, and to the diffusion of gases into one another, the writer has succeeded in arriving at certain regularities; these, however, it is desired to further investigate, before publication. In connection with the diffusion of gases, an experimental investigation is also planned, since the right kind of data appear to be lacking in this case.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 98.]

SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS. V. THE ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AND THE RELATIVE SPEED OF THE IONS IN THESE SOLUTIONS.[1]

BY CHARLES A. KRAUS

Received March 11, 1914

Introduction.

It was shown in the fourth paper of this series that the conduction process in solutions of the metals in ammonia is an ionic one. The positive carrier is identical with the positive ion of the salts of the same metal, while the negative carrier, which appears to be the same for different metals, can consist only of the negative electron e^-, either free or in association with ammonia. The characteristic properties of the metal solutions are due to the presence of the negative carrier.

With nonsoluble electrodes, such as platinum, the negative carrier passes into and out of the solution without observable material effects. That portion of the current which is carried through the solution by the negative carrier is, therefore, similar to the current in a metal, and in passing a current from a solution of one concentration to a solution of another concentration the only work involved is that of transferring the positive carrier.[2]

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[1] Previous papers of this series have appeared as follows: "I," THIS JOURNAL, 29, 1557 (1907); "II," *Ibid.*, 30, 653 (1908); "III," *Ibid.*, 30, 1197 (1908); "IV," *Ibid.*, 30, 1323 (1908). The sentence beginning on line 25, p. 1332 of the fourth paper should read: "According to this hypothesis, the negative carrier should move more *slowly* in dilute than in concentrated solutions,......"

[2] This is true for very dilute and very concentrated solutions. At intermediate concentrations the influence of the solvent envelope must be taken into account, as will be described below.

In the metal solutions, Faraday's laws do not hold true in their ordinary sense; for the passage of one equivalent of electricity is not accompanied by a transformation or transfer of one equivalent of matter. Under given conditions, the material change accompanying the current is a definite fraction of that predicted by Faraday's law. To be applicable to the metal solutions, Faraday's laws must be extended to include not only ordinary matter, but also such forms of matter as we find in the negative electron. Under this generalization, Faraday's law would merely state that, in a medium carrying a current, the amount of electricity passing a given cross-section is equal to the number of carriers crossing the section multiplied by the number of charges on one carrier and the value of the unit charge. This view is that commonly accepted in the present-day theories of metallic conduction.

In dilute solutions of the metals in ammonia we thus have what is equivalent to a mixture of metallic and electrolytic conduction. Of course, in these solutions, the negative electron is in all probability surrounded with an envelope of solvent molecules; however, the work involved in carrying solvent from a solution of one concentration to that of another, approaches zero as a limit as the dilution increases indefinitely.

It is the purpose of this paper to adduce further evidence as to the nature of the negative carriers in the metal solutions. If the hypothesis that the negative carrier is associated with ammonia in dilute solutions is correct, we should expect the negative carrier to possess a speed comparable with that of ordinary ions in ammonia. Moreover, we should expect that at higher concentrations the size of the envelope would decrease or even disappear entirely. Consequently its speed should increase at higher concentrations.

As was shown in the fourth paper of this series, the positive ions in the solution of a metal are identical with the positive ions of the salts of the same metal. As has been shown by the work of Franklin and Cady,[1] the speed of ordinary ions in ammonia does not change greatly with concentration. We may, therefore, determine the variation of the speed of the negative carrier as a function of concentration by comparison with the speed of the positive carrier.

The ratios of the mean speeds of two carriers present in a solution are usually determined by means of the moving boundary or of the Hittorf method. Unfortunately, such measurements in the metal solutions are extremely difficult. It was therefore determined to employ the method of measuring the electromotive force of concentration cells, which likewise involves the transference numbers of the ions. In the case of the solutions of the metals in ammonia, this method has much to recommend it; for not only does the electromotive force method make it possible to work with very small quantities of material over large ranges of concentration, but both anode and cathode constitute reversible electrodes which are peculiarly free from disturbances.

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[1] THIS JOURNAL, 26, 499 (1904).

Experimental.

Description of the Apparatus.—The apparatus employed in these experiments is outlined in Fig. 1. The solutions whose electromotive force was to be determined were prepared in the tubes *B* and *I*. These two tubes were connected by a tube, *M*, and the valve *L*. This valve was made by grinding a glass rod, *H*, into a conical seat in the glass tube at the bottom of *K*. The valve was polished with rouge and was quite impervious to liquids. A lubricant could not be employed. The plunger of this valve was sealed to a tube, *F*, of larger diameter, which was joined to the cell-arm *I* by means of a rubber tube, *G*. The greater portion of the rubber tube was covered with an impervious cement. No serious leakage was observed due to this connection. The valve was opened by raising the plunger *H* slightly. A clamp was provided to hold the plunger when desired. Normally, the valve was closed. The tube *B* was provided with a branch capillary, *N*, through which the metal was introduced in the manner described in previous papers.[1] The upper portion of the cell-arm *KI* consisted of a graduated tube which was calibrated with the plunger in position. The other cell-arm was provided with a narrower graduated tube, *A*, likewise calibrated. The volumes of the two cell-arms, up to fixed points on the graduated tubes, were determined. The lower portions of

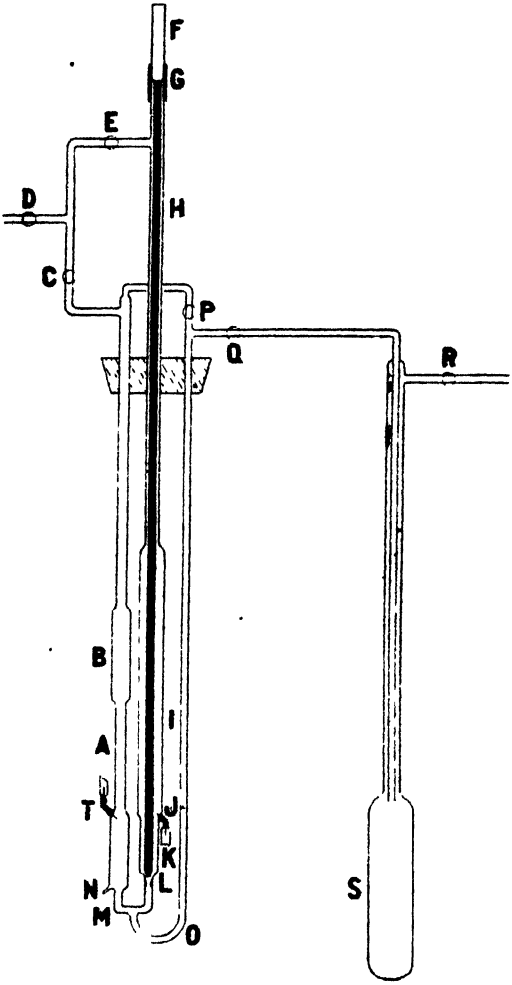

Fig. 1.

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[1] For a description of this operation, see THIS JOURNAL, 30, 1206 (1908).

the two cells each had a volume of about 4 cc. The tube *O*, which was joined to the bottom of the connecting tube *M*, was employed in changing the volume of the solution in the tubes *BI*. The electrode connections are shown at *JT*.

The procedure in manipulating the cell was somewhat as follows: After introducing the sodium, the cell was surrounded by boiling ammonia, connection was made through *DCE* with the source of ammonia, and liquid was condensed until its level reached the bottom of the smaller graduated tube *A*. The valve *L* was open in order that the liquid should be at the same level in both arms. The contents of the cell were thoroughly mixed. This was done by removing the bath, closing the cock *E*, and warming either of the tubes *BI* with the hand. The solution was thus driven into the other arm, and so back and forth until homogeneous. After replacing the bath, the volumes were read off on the graduated tubes when equilibrium had been established. Ammonia was now condensed into both tubes until the volume in the tube *KI* had been approximately doubled, the liquid levels being kept the same in the two arms. After mixing the solutions separately, the volumes were again read. Knowing the original volumes and the added volumes, it was possible to determine the relative concentrations of the solutions in the two tubes. The experiment was so carried out that the volumes were approximately in the ratio 1 : 2.

The cocks *CEP* being open, the valve *L* was opened cautiously, and the electromotive force was measured. In general, the level in *A* was originally kept a little below that in *I*, so that on opening *L*, solution from *I* ran into the connecting tube, and the contact between the two solutions was made at a point where mixing was a minimum.

After determining the electromotive force, the valve *L* was closed, as were also the cocks *EP*. The tube *S*, which had previously been exhausted, was surrounded with ammonia boiling under reduced pressure. When the temperature was well below the normal boiling point of ammonia, the cock *Q* was opened and the solution in *B* was forced out through the tube *O* by the pressure of its own vapor. When the solution had been transferred, the cock *Q* was closed and the cocks *PE* and valve *L* were opened. Half the solution in *I* now ran into *B*, after which *L* was closed and the volumes were read. The cocks *CDE* were opened and fresh ammonia was distilled into the cell as before. The ammonia in *S* was meanwhile evaporated through *R*, the sodium being left behind. After determining the liquid volumes, the valve was again opened and the electromotive force was determined as before. In this way the more concentrated solution always occupied the arm *B*, and the dilute solution of one experiment formed the concentrated solution of the next succeeding one.

A correction, of course, had to be applied for the volume of the small graduated tube *A*.

When the dilution had been carried sufficiently far, the entire contents of the cell were run into *S* and evaporated. The apparatus was exhausted, the tube *S* disconnected, and the metal was dissolved in alcohol. This solution was then washed out and titrated to determine the sodium. Thus all the data were obtained for determining the concentrations of the different solutions. After a series of experiments, the entire apparatus was taken down, washed, and dried. It was then set up again and operations carried out as before.

The electromotive force was determined by comparing with a standard cell, a sensitive galvanometer of 3000 ohms resistance serving as null instrument. The sensitiveness, of course, decreased in very dilute solutions where the resistance of the cell became comparable with that of the galvanometer. In the more concentrated solutions a change of 0.1 millivolt caused a deflection of about 6.0 scale divisions, while in the most dilute solutions it produced a change of only about 1.0 division. The percentage accuracy in the dilute solutions did not decrease in this proportion for the reason that the total electromotive force measured was greater in these solutions.

Although the electrodes employed were very small, the constancy of the electromotive force was remarkable. Within the limits of sensitiveness of the galvanometer, no fluctuations could be observed except in the most dilute solutions, where electrode effects appeared.

Calculations.—We have seen that, when a current passes through a metal solution, the metal is carried from anode to cathode. On the other hand, the anion apparently consists merely of a negative electron or of an electron associated with ammonia.

In the solution we have the equilibrium

$$M^+ + e^- \rightleftarrows Me$$

where M^+ is the positive ion, e^- the negative ion (consisting of the negative electron) and Me represents the neutral metal atom. According to the results of a previous paper, work is involved only in the transfer of the positive metal ions from one solution to another. Equating the osmotic and electrical work and solving for the electromotive force, we have

$$E_1 = \frac{2nRT}{F} \log_e \frac{(M^+)_1}{(M^+)_2}, \qquad \text{I}$$

where E_1 is the electromotive force of the cell due to the transfer of solute, F is the electrochemical equivalent, n is the fraction of the current carried by the positive carriers, R is the gas-constant, T the absolute temperature, and $(M^+)_1$ and $(M^+)_2$ are the activities of the positive ions in the two solutions, respectively.

As stated in the preceding section, the negative carrier consists of the negative electron, either free or associated with the solvent. The electrons themselves contribute nothing to the work of the cell. If, however, they are associated with the solvent, the solvent will be carried from a solution of higher to a solution of lower vapor-pressure. In concentrated solutions, we must, therefore, take this factor into account.[1] If m molecules of ammonia are associated with one electron, then for every equivalent of electricity, $m(1-n)$ mols of ammonia will be carried from the dilute solution of concentration c_2 and vapor-pressure p_2 to the concentrated solution of concentration c_1 and vapor-pressure p_1, the factor $1-n$ being the fraction of the current carried by the negative carrier. Since the negative carrier moves from the dilute to the concentrated solution, the solvent moves from higher to lower vapor-pressures, osmotic work is done, and the electromotive force due to the transfer of solvent will be in the same direction as that due to the transfer of metal. The solvent carried by the negative carrier will, therefore, contribute the electromotive force

$$E_2 = \frac{m(1-n)RT}{F} \log_e \frac{p_2}{p_1}. \qquad \text{II}$$

We are assuming here that the amount of ammonia associated with the carriers in the two solutions is constant, an assumption which must be very nearly true, since the concentrations differ only in the ratio of 1 : 2. The ammoniation of the metallic ions does not enter into the osmotic work, since the metal does not lose its solvent at the electrode; for the metal in any case remains in solution. The only factor introduced here is due to change in the ammoniation of the positive ion, which may be neglected. Moreover, it will be shown that, even if this were very large, it would not produce an appreciable result in the electromotive force of the cell.

We have, therefore, for the electromotive force E of the cell in the direction from solution 1 to solution 2,

$$E = E_1 + E_2 = \frac{2nRT}{F} \log_e \frac{(M^+)_1}{(M^+)_2} + m(1-n) \frac{RT}{F} \log_e \frac{p_2}{p_1} \qquad \text{III}$$

If the concentrations are made sufficiently small the activities $(M^+)_1$ and $(M^+)_2$ become equal to the concentrations M_1^+ and M_2^+, respectively, and the second term vanishes, since p_2 and p_1 approach equality.

We have then

$$E = \frac{2nRT}{F} \log_e \frac{M_1^+}{M_2^+}, \qquad \text{IV}$$

from which n, the transference number of the metal, may be calculated.

It has been shown in a preceding paper[2] that Raoult's law does not hold for solutions of sodium in ammonia at moderate concentrations. At these concentrations, therefore, Equation IV does not apply strictly. Nevertheless, it may reasonably be assumed that the equation will yield results of a correct order of magnitude. In dilute solutions, however, as will be shown in the next paper, the mass-action law applied to solutions of metals in ammonia. For these solutions, therefore, Equation IV is exact and the resulting value of n yields a precise measure of the transference number of the metal ion.

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[1] Lewis, THIS JOURNAL, 30, 1355 (1908)

[2] *Ibid*, 30, 1197 (1908).

As we shall see presently, the transference numbers of the carriers in the more concentrated solutions change rapidly with concentration. This factor also has been neglected in the preceding equation. It does not seem worth while to introduce a correction term for this factor, since so many other uncertainties underlie the application of the equation to concentrated solutions. The values obtained for n may be looked upon as mean values between the concentrations in question. Throughout the experiments the concentration ratio of approximately 1 : 2 was maintained between the solutions measured. Over this concentration-interval the ionization does not change greatly, so that the ratio of total salt concentrations may be employed in place of the ratio of ion concentrations. When the conditions of experiment warrant a greater precision, a correction will later be made.

It has also been assumed that the equilibrium existing in the solution is that of a binary electrolyte. The correctness of this assumption will be shown in another paper.

Experimental Results.—The results obtained in three independent series of experiments are embodied in the following table. The first column gives the number of the observation; the second and third columns give the concentration of the solutions in the cell, while the fourth column gives the logarithm (to the base 10) of the ratio of these concentrations. Under c_a is given the mean concentration of the two solutions and under $E \times 10^3$ the observed electromotive force in millivolts. Finally, in the seventh column, are given the values of the ratio $(1 - n)/n$, where n is the transference-number of the sodium ion Na^+, calculated from Equation IV, the absolute temperature being 240°.

Discussion.

The fraction of the current carried by the positive carrier Na^+ is n. That carried by the negative carrier is $1 - n$ and the ratio $(1 - n)/n$ is the ratio of the amount of the current carried by the negative carrier to that carried by the positive carrier. It is to be noted that in the case of the negative carrier this ratio does not necessarily represent the speed of any one negative carrier relative to that of the positive carrier, for the speed of all the negative carriers is not necessarily of the same order of magnitude. The ratio, therefore, involves the average value for all

TABLE I.—RELATION BETWEEN ELECTROMOTIVE FORCE AND CONCENTRATION.

No	C_1	C_2	$\log c_1/c_2$	c_a	$E \times 10^2$	$(1-n)/n$
			Experiment I.			
1	0.4660	0.1928	0.3741	0.325	0.85	41.0
2	0.1770	0.0863	0.3123	0.131	0.96	39.0
3	0.0805	0.0460	0.2434	0.063	1.00	21.4
4	0.0420	0.0148	0.3274	0.031	1.40	20.6
5	0.0177	0.0065	0.4373	0.012	2.55	15.0
			Experiment II.			
2	0.7628	0.3390	0.3522	0.551	0.609	54.0
3	0.3020	0.1892	0.2029	0.295	0.491	38.2
4	0.1625	0.0897	0.2580	0.126	0.790	32.0
5	0.0837	0.0490	0.2322	0.066	0.867	24.4
6	0.0447	0.0222	0.3046	0.033	1.355	20.4
7	0.0205	0.0121	0.2307	0.016	1.300	15.4
			Experiment III			
1	1.014	0.6266	0.2344	0.870	0.080	277.6
2	0.9738	0.4693	0.3100	0.732	0.328	90.6
3	0.4571	0.3181	0.1525	0.387	0.336	42.2
4	0.4339	0.2310	0.2739	0.335	0.620	41.2
5	0.2224	0.1600	0.1437	0.191	0.384	34.6
6	0.2135	0.1153	0.2074	0.164	0.72	33.4
7	0.1109	0.0770	0.1580	0.094	0.50	29.2
8	0.1064	0.0570	0.2690	0.081	0.86	28.8
9	0.0548	0.0376	0.1639	0.046	0.65	23.2
10	0.0526	0.0274	0.2934	0.040	1.07	25.0
11	0.0263	0.0180	0.1510	0.023	0.78	17.4
12	0.0253	0.0140	0.2570	0.020	1.38	16.4
13	0.0135	0.0091	0.1582	0.011	0.92	11.4
14	0.0130	0.0070	0.2058	0.010	1.80	13.2
15	0.0065	0.0034	0.2779	0.0050	2.60	9.2
16	0.0031	0.0016	0.2883	0.0024	3.40	7.0

the negative carriers present. In the case of the sodium ion we may safely assume that all the ions move with the same mean speed, and that the speed is independent of concentration. Any variation of the ratio, therefore, represents the change in mean speed of the negative carriers.

In Fig. 2, the values of the ratio $(1 - n)/n$ are plotted as ordinates against those of the logarithms of the mean dilution (log $1/c_a$) as abscissae. The different points are in excellent agreement, both for points of the same and of different series. This shows that the results obtained are reproducible and represent equilibrium conditions. Such variations as appear are due partly to experimental error and partly to the approximations underlying the calculations.

It will be seen on inspection that in dilute solutions the negative carrier carries about seven times as much current as the positive carrier. The fraction of the current carried by the negative carrier increases with concentration, particularly as normal concentration is approached. In the most concentrated solutions (mean concentration 0.87 normal) the negative carrier carries approximately 280 times as much current as the positive carrier. In other words, the relative amount of current carried by the negative carrier at this concentration is 40 times as great as that at high dilutions.

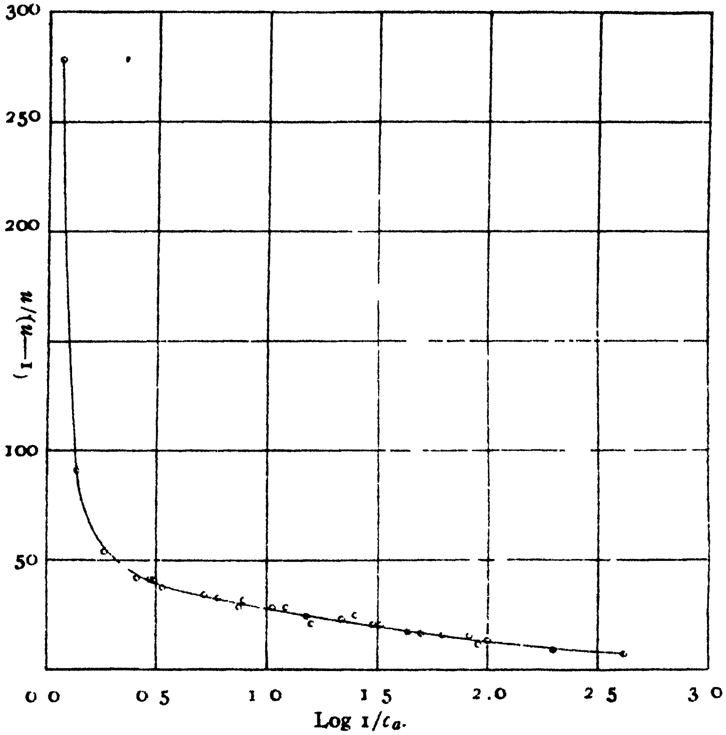

Fig 2 —Showing change of $(1 - n)/n$ with the concentration

The values of $(1 - n)/n$ are, of course, affected to some extent by the approximations made in the calculations. The ionization is changing with concentration, so that, even at the highest dilutions, the concentration ratio c_1/c_2 is somewhat greater than the ratio $c_1\gamma_1/c_2\gamma_2$ of the ion-concentrations. The error due to this source is negligible in comparison with the observed change in the ratio $(1 - n)/n$. At higher concentrations the ionization of electrolytes does not follow the mass-action law. This error also is small in comparison with the change observed in this ratio. As to order of magnitude, therefore, the values of $(1 - n)/n$ are doubtless correct.

It follows, then, that the fraction of the current carried by the negative carrier increases enormously with increasing concentration. This shows that the mean speed of this carrier increases greatly with increasing concentration.

In dilute solutions the value of $(1 - n)/n$ appears to be approaching a definite limit which is probably not far from 7, the lowest value measured. The ionic conductance due to the sodium ion as deduced from conductance and transference measurements is 130.[1] The conductance of the negative carrier in a sodium solution is, therefore, $7 \times 130 = 910$, and therefore the molecular conductance of sodium at zero concentration is 1040. As will be shown in another paper, this is in excellent agreement with the directly measured value.

Since, in dilute solutions, the speed of the negative carrier is of the same order of magnitude as that of the sodium ion, it follows that the negative carrier must be associated with solvent molecules. In concentrated solutions, where the vapor-pressure lowering due to the solute becomes appreciable, the solvent associated with the negative carrier has an appreciable influence on the electromotive force, and a maximum value of the number of solvent molecules (m) associated with one negative carrier can be calculated. It can thus be shown that a portion of the current is carried by carriers not associated with the solvent. Namely, by placing n equal to zero in Equation III we may calculate a maximum value of m from the measured electromotive force (0.080 volt) of the pair of solutions used in Expt. III, No. 1, where the two concentrations are 1.014 and 0.627 normal, and where the ratio of the two vapor-pressures is 1 : 1.006.[2] The value so calculated is 0.67. The assumption that n is zero implies, of course, that there is *no* transference of the positive ion, and, therefore, that the whole electromotive force corresponds to the work done in the transference of ammonia. Since this assumption, even in the more concentrated solutions, is not strictly true, the value of m is doubtless considerably less than 0.67, but it can not be greater than this. This fact shows that at least one-third of the current is carried by electrons which are not associated with solvent, since those that are so associated must carry at least one molecule of ammonia.

Moreover, it is evident from the table that, at higher concentrations, the electromotive force approaches zero, or at least a very small value, as a limit. If one molecule of ammonia were associated with a single electron, a very considerable electromotive force would necessarily result, since the vapor-pressure of the solution changes rapidly with concentration.[2] The greater portion of the current is, therefore, carried by negative carriers which are wholly unassociated with ordinary matter. Doubtless, except in the case of very concentrated solutions, the larger proportion of the negative electrons is associated with ammonia; but their speed under a given potential gradient is relatively so small that they contribute but little to the conducting power of the solution.

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[1] Kraus and Bray, THIS JOURNAL, 35, 1368 (1913).

[2] *Ibid.*, 30, 1210 (1908).

We are now able to form a very good picture of the process by which conduction takes place in the solutions of metals in ammonia. As we have seen, the metal dissociates in solution according to the equation

$$Me = M^+ + e^-,$$

where Me represents the neutral atom of metal which is to be looked upon as a combination between the positive metal ion M^+ and the negative electron e^-. For the alkali metals both ions M^+ and e^- are univalent as will be shown in a later paper. The process of ionic dissociation obeys the mass-action law, so that

$$\frac{(M^+)(e^-)}{(Me)} = K,$$

where the symbols in parentheses represent the activities of the different molecular species, which may be replaced by the concentrations themselves in dilute solutions. It is probable that both the metal ions M^+ and the neutral metal molecules Me are ammoniated to a greater or less extent. That the electrons e^- are associated with ammonia in dilute solutions can not be doubted, for the ratio of the mobilities of the two ions Na^+ and e^- approaches a limiting value lying in the neighborhood of 7.[1]

Since the viscosity of the solution does not change materially with the concentration, the change in speed of the negative electron can not be due to viscosity change. But if the electrons are associated with ammonia, then, as soon as the activity of the solvent becomes sensibly constant, the ammoniation of the electron becomes sensibly constant, and the speed being determined by the friction of the ionic envelope with the solvent molecules, the mobility remains constant.

As the concentration increases, the size of the ionic envelope must diminish and since the frictional resistance diminishes with the size of the envelope the mobility of the negative carrier increases. But this is not a complete description of the processes involved as the concentration of the solution increases. The speed of an electron associated with only one molecule would not be greatly different from that of an electron associated with a larger number of molecules. Since the current carried by the negative carrier increases at least 40 times, when the concentration changes from about 0.001 normal to normal, a mere change in the size of the envelope will not suffice to account for the increased carrying capacity of the negative ions. What takes place as the concentration becomes greater is that a portion of the electrons are completely freed from ammonia for a fraction of the time. No individual electron is free for any considerable length of time, but the free electrons, the solvent, and the solvated electrons are in kinetic equilibrium. In concentrated solutions we have, in fact, three carriers present, namely: Na^+, $e^-(NH_3)_x$, and e^-. When free from ammonia, the electrons possess a mobility comparable with that of the electrons in a metal. A very small number of free electrons will, therefore, suffice to produce an enormous increase in the carrying capacity of the negative carriers in solution. The great increase in the proportion of current carried by the negative carrier is thus due to the presence of a small number of free negative electrons.

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[1] Compare Kraus, THIS JOURNAL, 36, 35 *et seq.* (1914).

The free electrons on reaching the electrodes pass into it freely and produce no material change in state in this process. The process of conduction from the solution to the electrode is thus like that in the metal itself in that it consists entirely in a motion of the electrons.

On the basis of these considerations, we are able to predict what will be the properties of very concentrated solutions of the metals in ammonia. The number of electrons, which at any instant possess no envelope of ammonia in a solution of metal at normal concentration, is very small and they possess a mobility many hundred times greater than that of the metal ion. As the solution becomes more concentrated, the number of electrons free from ammonia will finally be comparable with the number of sodium ions present. As a result, such solutions must possess a conducting power many hundred times greater than that of a normal solution of sodium in ammonia. If such is the case, these solutions should begin to approach the metals in conducting power. If the properties of metals are due to the presence of free electrons, it follows that, since concentrated solutions of the metals contain these electrons, these solutions should exhibit those properties which are characteristic of metals. In another paper I shall show that this is the case.

The negative carrier present in dilute solutions of the metals in ammonia possesses considerable interest. The fact that this carrier possesses a speed approximately seven times that of the sodium ion indicates that the solvent envelope surrounding the negative electron is relatively small. It is interesting to note that the speed of the negative electron in ammonia is many times greater than that of the negative ion produced by radiations in hexane.[1] The dielectric constant of ammonia is much greater than that of hexane and it is not unlikely that the greater speed in ammonia is a consequence of this circumstance, for the higher the dielectric constant of the medium, the smaller will be the field of force due to the electric charge.

Let us now consider what takes place around an electrode when a current passes continuously through the solution of a metal in ammonia. At the cathode the concentration of metal is increased under the action

[1] THIS JOURNAL, 36, 59 (1914).

of the current. As soon as such concentration increase reaches an appreciable value, a relatively smaller quantity of metal is carried up for a given current. Consider a number of equipotential surfaces in the neighborhood of the cathode at which the concentration of the metal increases as the cathode is approached. The amount of metal carried across these surfaces decreases in proportion to the decrease of the transference number of the metal ion as the electrode is approached. There is, thus, a distributed accumulation of the metal throughout the volume of the solution in the neighborhood of the electrode. In the end, if the current be sufficiently great, no further change will take place immediately at the electrode surface. At a distance from the electrode the concentration change will increase up to a certain point and then again decrease until the normal concentration of the solution is reached.

The metal, then, is not deposited at the electrode surface, but is distributed throughout the electrode volume. Of course, the phenomenon is modified by diffusion and, under certain conditions, by convection. It is also greatly influenced by concentration. At very high concentrations the phenomena are much less marked than at low concentrations. The phenomena described in the fourth paper of this series are completely accounted for by the above hypothesis.

At the anode, with a non-soluble electrode, the phenomenon differs greatly from that at the cathode, if the solution is not too concentrated. Assume an electrode surrounded by a dilute solution of given concentration. When an electromotive force is applied, the negative carriers move to the electrode while the positive carriers move away from it. Now, the negative carrier moves up to the anode and then enters the metal. The only physical change accompanying this process is that ammonia is left behind at the electrode surface. In a dilute solution the ammonia thus left behind is relatively so small that it has no material influence on the observed phenomena. At the electrode surface there is, therefore, no manner of mechanical disturbance and we are able to observe phenomena which in ordinary solutions would be obscured by secondary effects.

The withdrawal of positive metal ions from the immediate vicinity of the anode surface causes an almost instantaneous removal of all metal from this region. The speed of this process is accelerated owing to the fact that when the concentration change sets in, the potential gradient in this region rises and thus increases the speed of the carriers.

In the immediate neighborhood of the anode there will, therefore, result a region which contains no metal whatever and across which the current is carried entirely by the negative carriers moving freely under the action of the applied potential. The extent of this region will depend on the electromotive force applied, the concentration of the solution, the shape and size of the electrodes, and other specific factors. As was described in the fourth paper of this series, the boundary of the metal-free region is usually very clear and distinct. Up to this boundary the metal is maintained in position by processes of diffusion and convection, the latter factor being the most important if a considerable potential is applied.

It is thus seen that in the case of an anode in a dilute metal solution, where one of the carriers is removed from solution when it reaches the electrode surface, the current is carried entirely by one carrier over an appreciable distance. That a similar phenomenon obtains in solutions of ordinary electrolytes appears highly probable.

Summary.

The electromotive force of concentration cells of solutions of sodium in liquid ammonia has been measured over an extended concentration range.

From these measurements approximate values of the transference numbers have been calculated for different concentrations. The ratio $(1 - n)/n$ of the fraction of the current carried by the negative and positive ions approaches a limiting value of approximately 7 in dilute solutions, and increases to a value of 280 at a mean concentration somewhat less than normal.

Assuming the speed of the positive ion to remain constant, the mean speed of the negative ion increases 40 times between about 0.001 and 1.0 normal. Assuming the equivalent conductance of the positive ion to be 130 (that of the sodium ion), the equivalent conductance of the dilute metal solution is calculated to be 1040.

These results are accounted for on the assumption that the ions Na^+ and e^- exist in solution. At high dilutions the negative electron e^-, which serves as negative ion, is surrounded by an envelope of ammonia which determines its speed. At higher concentrations some of the negative electrons are free from the ammonia envelope for a fraction of the time Under these conditions they move with a speed comparable with that of the negative electrons in metals. This accounts for the rapid increase of the transference number of the negative carrier at higher concentrations, for the number of free electrons increases as the proportion of metal to ammonia increases.

The electrode phenomena described in the fourth paper of this series are in accord with the above hypothesis.

On the basis of the osmotic work involved, it is shown that in the most concentrated solutions a portion of the current is carried by carriers not associated with ordinary matter.

BOSTON, MASS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS, PUBLICATION NO. 16.]

THE MECHANISM OF THE CATALYSIS OF THE DECOMPOSITION OF HYDROGEN PEROXIDE BY COLLOIDAL PLATINUM.

BY DUNCAN A. MACINNES.

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As an explanation of the catalytic effect of colloidal platinum on the decomposition of hydrogen peroxide, Bredig[1] and his associates accept the hypothesis, originally advanced by Haber,[2] that the platinum first forms an unstable oxide, which reacts with the peroxide giving, of course, oxygen and water. The possibility of such an intermediate product has appeared more probable since the work of Grube,[3] who has shown that the evolution of oxygen from a platinized platinum cathode is preceded by the formation of PtO_3. The two stages in the reaction, according to this explanation, may be represented by the equations:

$$x\text{Pt} + {}^1/_2\, y\text{O}_2 = \text{Pt}_x\text{O}_y \qquad (1)$$

$$\text{Pt}_x\text{O}_y + y\text{H}_2\text{O}_2 = x\text{Pt} + y\text{H}_2\text{O} + y\text{O}_2 \qquad (2)$$

If the concentration of the unstable oxide remains constant, or, in other words, if the change represented by equation (1) is rapid in comparison with that represented by equation (2) the reaction would be expected to be of the first order. That this is only approximately true is evident from the typical series of determinations from the work of Bredig and Ikeda[4] given in Table I. Time in minutes is given under the columns headed t and under $(a - x)$ the concentrations of hydrogen peroxide in arbitrary units. The columns headed by k_1 contain the value of the expression: $1/t \log a/(a - x)$ the first order "constant." In this formula

TABLE I.

t.	$a - x$.	$k_1 \times 100$.	$K_m \times 100$.	t.	$a - x$.	$k_1 \times 100$.	$K_m \times 100$.
0	12.54	..	..	0	11.80	..	..
4.12	8.57	4.01	2.96	3.90	8.30	3.93	2.87
7.37	6.19	4.15	2.97	7.90	5.70	4.00	2.81
12.25	3.68	4.37	2.95	11.96	3.70	4.22	2.84
19.75	1.52	4.62	2.89	16.55	2.04	4.60	2.94

t.	$a - x$.	$k_1 \times 100$.	$K_m \times 100$.
0	10.50	..	..
3.82	7.43	3.93	2.80
9.29	4.50	3.95	2.68
15.37	2.27	4.26	2.74
19.80	1.37	4.45	2.70

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[1] "Anorganische Fermente," *Z. physik. Chem.*, **31**, 258 (1899) and **37**, 5 (1901).

[2] *Z. anorg. Chem.*, **18**, 40 (1898).

[3] *Z. Elektrochem.*, **16**, 621 (1910).

[4] *Z. physik. Chem.*, **37**, 5 (1901).

a represents the concentration of the peroxide at the beginning of the reaction. It is apparent that the value of the first order "constant" increases as the reaction proceeds. This slow increase of k_1 is also quite evident in fifty other series in the paper from which these figures are taken.

That this shift in the value of k_1 is not caused by a slow saturation of the catalyzer with oxygen is definitely shown by some experiments of these authors, the data of which are given in Table II. The colloidal platinum used in Series B had already been used in Series A and contained, presumably, the full quantity of the unstable oxide. A similar increase in the value of k_1 can be observed in both series. This means, of course, that if the reaction takes place in the stages represented by equations (1) and (2) the process represented by equation (1) is much the more rapid. We must, therefore, seek another explanation of this interesting variation.

TABLE II

	Series A Conc Pt 0.000014				Series B Conc. Pt 0.0000084		
t	$a - x$	$100k_1$	$K_m \times 100$	t	$a - x$.	$100k_1$	$K_m \times 100$
0	20.3			0	39.6	..	..
5.93	15.8	3.72	3.45	5.9	29.2	2.25	2.07
10.90	9.3	4.13	3.30	12.5	19.1	2.54	2.25
16.00	4.8	4.62	3.46	18.4	13.1	2.61	2.25
				25.1	7.9	2.79	2.28
		Mean.	3.40	30.3	5.3	2.89	2.28
						Mean,	2.23

As the colloidal platinum presents a very large surface to the liquid it seems possible that an adsorption of the peroxide on this surface influences the rate of reaction. It is also probable that the reaction is confined to a layer next the solid-liquid boundary.[1] Such an adsorption would be expected to follow the usual isotherm

$$x/m = \alpha(c - x)^n, \tag{3}$$

in which x, c and m are respectively the amount of adsorbed solute, the total concentration of solute and the concentration of the colloid, and α and n are constants. The term $(c - x)$ represents the concentration of solute in equilibrium with the adsorbed quantity x. It can easily be seen that if the exponent n is less than 1, which is the case in adsorption isotherms which have been directly measured, a relatively larger portion of the total amount of the solute will be adsorbed from dilute solutions, and if the reaction takes place in the adsorbed layer, the adsorbing medium will be more effective as a catalyst as the concentration decreases, as is observed in the case under discussion.

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[1] Freundlich ["Kapillarchemie" (p. 382)] has suggested adsorption and diffusion through the adsorbed layer as an explanation of this variation

If the adsorbing material is very dilute, the amount of adsorbed substance x may be neglected where it occurs in the difference $(c - x)$. The adsorption isotherm then takes the form:

$$x/m = \alpha c^n \qquad (4)$$

Solving for x and substituting it in the place of the active concentration c in the differential equation of a reaction of the first order, $dc/dt = K'c$, we obtain:

$$dc/dt = K'm\alpha c^n \quad \text{or} \quad dc/c^n = K'm\alpha dt$$

Integrating between the time limits zero and t the expression becomes:[1]

$$C_o^{1-n} - C_t^{1-n} = [(n - 1)K'm\alpha]t,$$

and collecting all the constants in the term K we have

$$C_o^{1-n} - C_t^{1-n} = (Km)t, \qquad (5)$$

in which C_o and C_t are the concentrations of peroxide at the beginning of the reaction and after the elapse of the time t, respectively.

The amount of substance adsorbed will depend on the extent of the surface of the adsorbing medium exposed to the solution. The surface will, of course, vary with the concentration of the adsorbent (m of Eq. 3) and its degree of dispersion, a factor which influences the value of α in the same equation. Since the term Km (of Eq. 5) is a product containing α as one of its factors it would, in general, be a constant for more than one series only when a given concentration of the identical preparation of colloid is used in all the runs. There is, however, no such restriction as to the constancy of the term n for its value depends only on the nature of the substances involved. If Equation 5 is based on correct assumptions the value of this constant found for one series of determinations should hold also for any other series. Calculations, by the author, based on the work of Bredig and Ikeda have shown that this is the case. A single value (0.8) for the adsorption exponent has been found sufficient to ex-

TABLE III.

C_{Pt} 0.0000103.

t.	$a - x$.	100 k_1.	100 (K_m).
0	24.8	..	..
2.32	20.25	3.8	(3.28)
4.52	16.4	4.0	3.34
7.62	11.82	4.2	3.44
9.67	9.38	4.4	3.48
12.2	7.3	4.4	3.42
14.7	5.4	4.5	3.40
17.2	3.55	4.9	3.56
19.0	2.8	5.0	3.54
22.0	1.91	5.1	3.46

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[1] Bodenstein and Stock (*Ber.*, 40, 570) have applied a similar equation to the catalysis of gas reactions.

press the experimental results of these investigators, even though the concentration of the colloid and the initial concentration of the hydrogen peroxide vary through rather wide limits. A glance at the columns headed Km in Tables I, II and III which contain values of this product will indicate how closely the equation expresses the results.

The values of Km found in Table II are particularly interesting since they afford another test of the validity of the assumptions contained in the derivation of Equation 5. As will be recalled, the same sample of colloid was used in Series A and B but at different concentrations. In this case the ratio of the two constants $(Km)_B/(Km)_A$ should be the same as the ratio of the concentrations of the colloid $(m_B)/(m_A)$. The values actually observed are:

$$\frac{(Km)_B}{(Km)_A} = \frac{2.23}{3.40} = 0.65 \text{ and } \frac{m_B}{m_A} = \frac{0.0000084}{0.0000140} = 0.60,$$

which agree as closely as could be expected.

An equation that does not involve the neglecting of the term x, where it occurs in the difference $(c - x)$, in the adsorption isotherm, can be derived, but it is, in its simplest form, a three-constant expression. As we have no independent means of evaluating the extra constant, the use of such an equation would give no further light on the mechanism of the reaction. The great dilution of the catalyst (not over 0.000031 mol per liter in any case investigated) lends support to the supposition that we are dealing with a rapid reaction in an adsorption layer which involves only a small portion of the total concentration.

In the foregoing, only the series in which pure hydrogen peroxide and the colloid are in solution are considered. Equation 5 does not describe the results of experiments in which "poisons" such as prussic acid, iodine or hydrogen sulfide are present, since there are a number of ways in which such substances may influence the reaction, such as chemical combination of the "poison" with the platinum or with the peroxide, selective adsorption of the "poison," etc. It is interesting to note that the reaction under consideration is one of the very few in which this test for adsorption can be used, since practically all other reactions give rise to products which will change the system as the reaction proceeds.

It also seems probable in the light of these calculations that the diffusion of the peroxide to the surface of the colloid, *i. e.*, the velocity of adsorption, is more rapid than the rate with which the decomposition takes place. The Brownian movement of the particles and the stirring effect of the bubbles of evolved oxygen undoubtedly have the effect of bringing fresh solution into contact with the colloidal particles, thus maintaining a saturated adsorption layer.

URBANA, ILL.

HYDROGEN TELLURIDE AND THE ATOMIC WEIGHT OF TELLURIUM.

By L. M. Dennis and R. P. Anderson.

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1. Introduction.

The position of tellurium in the Mendeléeff arrangement of the elements is, in respect to the atomic weight of the element, strikingly anomalous, and has given rise to ingenious speculations and many experimental investigations that have had as their object the explanation or the removal of this anomaly. Contributions that have been made to the chemical literature upon this subject up to the year 1911 have been summarized by Dudley and Jones.[1] Since that time a further article by Flint[2] has appeared, in which the author states that no variation in the atomic weight of tellurium was obtained when his method of hydrolytic precipitation was used on crude material. Pellini[3] tested the method of Browning and Flint,[4] and as a result of numerous analyses concludes that this method offers no evidence of a decomposition of tellurium. The same conclusion concerning the method of Browning and Flint has been reached by Morgan.[5] In this connection it is interesting to note that while so many investigators have been endeavoring experimentally to demonstrate the complexity of tellurium, and thus to furnish an explanation of its high atomic weight, Kusnezow[6] suggests that the atomic weight now assigned to the element may, after all, not be abnormal even though it is higher than that of iodine.[7] He bases this idea upon certain variations in the atomic weights in the elements of the uneven series, but the data that he cites do not appear strongly to support the validity of his suggestion.

If the high atomic weight of tellurium is due to the presence of a small amount of an element that is analogous to the members of the primary group of Group 6 of the Mendeléeff table, it seems reasonable to suppose that this substance might be separated from what is now termed tellurium by some process of fractionation, a method that has yielded such excellent results in the separation of other markedly similar elements and compounds. Mendeléeff predicted[8] the existence of such an element, giving it provisionally the name dvi-tellurium and assigning to it an atomic weight of 212. If, however, such an element exists, its atomic weight is probably somewhat greater than this value. The elements in the odd series of Groups 4 and 5 of the Periodic Table show the following differences in their atomic weights:

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[1] This Journal, 34, 995 (1912).

[2] *Ibid.*, 34, 1325 (1912).

[3] *Atti R. Accad. Lincei*, [5] 21, I, 218 (1912).

[4] *Am. J. Sci.*, [4] 28, 347 (1909).

[5] This Journal, 34, 1669 (1912).

[6] *Iswestja des Donschen Polytechn. Inst. zu Nowotscherkask*, 1, II, 380 (1912); *Chem. Zentralb.*, 84, I, 772 (1913).

[7] See also Werner, *Ber.*, 38, 914 (1905).

[8] *J. Chem. Soc.*, 55, 649 (1889)

Series.	Group 4 At. wts.	Differences.	Group 5. At wts.	Differences
3............ ...	Si 28.3		P 31.04	
		44.2		43.92
5.......... .. .	Ge 72.5		As 74.96	
		46.5		45.24
7.......... . .	Sn 119.0		Sb 120.2	
		88.1		87.8
11..... .	Pb 207.1		Bi 208.0	

It is seen that in each group the difference between the atomic weight of the element in the 7th series and that of the element in the 11th series is very nearly twice (1.99 times) as great as the difference between the atomic weights of the elements in the 3rd and 5th series in that group. If this holds true for the 6th group as well, the atomic weight of dvi-tellurium would be equal to twice the difference between the atomic weights of selenium and sulfur, or 2 × 47.13 = 94.26, plus the atomic weight of tellurium. If the atomic weight of tellurium is 127.5, the present value, the atomic weight of dvi-tellurium would be about 127.5 + 94.3 = 221.8. If the atomic weight of tellurium is less than that of iodine, say 126.5, dvi-tellurium would then have an atomic weight of about 126.5 + 94.3 = 220.8. In this latter case, what is now known as tellurium would consist of 98.94% of true tellurium and 1.06% of dvi-tellurium.

If this dvi-tellurium is really the cause of the high atomic weight, it seems reasonable to suppose that, even though it is present in comparatively small amount, it should, by reason of its much higher atomic weight, be rather easily separable from tellurium. The failure of so many able investigators to resolve tellurium into two or more components would appear to support the view that the high atomic weight of the substance is, as has been suggested by others, due rather to the presence of a comparatively large amount of a body that resembles tellurium very closely and that possesses an atomic weight but slightly above that of tellurium. If this were the case, the lack of success in the attempts to separate the two substances might readily be understood, for the history of the separation of the chemical elements furnishes more than one illustration of such a case. For example, the composite nature of didymium was suggested by Marignac as long ago as 1853, and the same idea was later advanced by Delafontaine and by Brauner. Nevertheless many investigations and many methods of extended fractionation failed to yield any distinct components of didymium until Auer von Welsbach, by the use of a method that had been suggested by Mendeléeff, succeeded, in 1885, in splitting didymium into praseodymium and neodymium. He accomplished this result because he employed a method of fractionation that was practically new, and also because he started with a large amount of material which he subjected to many hundred fractional crystallizations.

If tellurium is really of composite nature, and if it consists of two elements of closely similar properties, the work that already has been done upon this subject would seem to demonstrate that the fractional separation of these components will be successful only (*a*) if the procedure that is used yields quite rapid and complete separation of the two substances, or (*b*) if a very large number of fractional separations is made with large amounts of material.

The methods of fractionation that have thus far been employed in the attempt to split tellurium into components are:

1. The distillation of tellurium.[1]
2. The distillation of tellurium dioxide.[2]
3. The distillation of tellurium tetrachloride.[3]
4. The sublimation of tellurium tetrabromide in a vacuum.[4]
5. The crystallization of hydrated telluric acid, $H_2TeO_4.2H_2O$.[5]
6. The crystallization of potassium tellurium bromide, K_2TeBr_6.[6]
7. Crystallization of barium tellurate.[3]
8. The precipitation of tellurium from a solution of tellurium in potassium cyanide by a current of air.[4]
9. Precipitation of sodium thiotellurate.[7]
10. Hydrolysis of a hydrochloric acid solution of tellurium tetrachloride.[8]
11. Precipitation of tellurium from a solution of tellurium tetrachloride by hydrazine hydrochloride.[9]
12. Electrolysis of tellurium tetrabromide and tetrachloride.[3]
13. Decomposition of hydrogen telluride.[3]

The results of most of these methods of fractionation have been such as to lead to the conclusion that tellurium is homogeneous and that the anomalously high atomic weight of the element must be regarded as correct. It has seemed, however, to the authors of this paper that, before such a conclusion is accepted as final, further attempts should be made to decompose tellurium; for it is still possible that, as has been pointed out above, a new method of fractionation may give positive results although the methods heretofore in use have failed to do so. In choosing a procedure, it seemed to us that the fractional distillation of a gaseous compound of tellurium offered the best promise of success, and of such compounds hydrogen telluride was selected.

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[1] Baker and Bennett, *J. Chem. Soc.*, 91, 1849 (1907).

[2] Baker and Bennett, *J. Chem. Soc.*, 91, 1849 (1907); Marckwald, *Ber. d. chem. Ges.*, 40, 4730 (1907); Norris, THIS JOURNAL, 28, 1675 (1906).

[3] Baker and Bennett, *Loc. cit.*

[4] Brauner, *J. Chem. Soc.*, 55, 382 (1889).

[5] Staudenmaier, *Z. anorg. Chem.*, 10, 189 (1895); Baker and Bennett, *J. Chem. Soc.*, 91, 1849 (1907); Marckwald, *Ber. d. chem. Ges.*, 40, 4730 (1907).

[6] Norris, Fay and Edgerly, *Am. Chem. J.*, 23, 105 (1900).

[7] Brauner, *J. Chem. Soc.*, 67, 549 (1895); *Chem. News*, 71, 196 (1895).

[8] Brauner, *J. Chem. Soc.*, 55, 382 (1889); Baker and Bennett, *Loc. cit.*; Browning and Flint, *Am. J. Sci.*, [4] 28, 347 (1909); Flint, *Ibid.*, [4] 30, 209 (1910); Harcourt and Baker, *J. Chem. Soc.*, 99, 1311 (1911); Flint, THIS JOURNAL, 34, 1325 (1912); Pellini, *Atti R. Accad. Lincei, Roma*, [5] 21, I, 218 (1912); Morgan, THIS JOURNAL, 34, 1669 (1912).

[9] Dudley and Jones, THIS JOURNAL, 34, 995 (1912)

Both Metzner[1] and Baker and Bennett[2] have determined the atomic weight of tellurium that was prepared by the decomposition of hydrogen telluride, but the systematic fractional distillation of hydrogen telluride does not appear to have previously been attempted.

Hydrogen telluride dissociates at a much lower temperature, 0°, than either of its analogues, hydrogen sulfide and hydrogen selenide. It may logically be inferred, therefore, that the hydride of a higher member of the group, such as the hypothetical dvi-tellurium, would break down at a temperature considerably below 0°, and that, if a mixture of the hydrides of tellurium and dvi-tellurium in solid form were prepared with the aid of liquid air and were then allowed gradually to rise in temperature, there might result not only the decomposition of tellurium through the fractional distillation of its hydride, but also the segregation, in the distilling flask, of dvi-tellurium because of the breaking down of its hydride before the boiling point of hydrogen telluride, 0°, was reached.

2. Purification of Material.

The material that was used in this investigation comprised 500 g. of "pure" tellurium from C. A. F. Kahlbaum, Berlin, and about 1400 g. of tellurium of a purity of approximately 85% from the American Smelting and Refining Company.

In the purification of this material the method of Staudenmaier[3] was rather closely followed. The tellurium was dissolved in a slight excess of nitric acid (1 : 1) and there was then added a slightly greater amount of chromium trioxide than was needed to oxidize all of the tellurium to the hexavalent state. The resulting solution was concentrated by evaporation on a water bath until the greater part of the telluric acid was precipitated. This telluric acid, still moist with adhering nitric acid, was placed in a funnel and washed with alcohol. The alcohol reduces the chromium trioxide to chromic oxide which then forms chromic nitrate with the nitric acid that is present and this is removed by the alcohol. Washing with alcohol was continued until the alcohol took on no color, and the telluric acid was then further purified by repeatedly dissolving it in hot water and precipitating it with concentrated nitric acid. The pure white telluric acid thus obtained was placed in a Büchner funnel, and was washed with absolute alcohol to remove the nitric acid. In this manner about three kilograms of telluric acid that gave no test for either sulfur or selenium was prepared.

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[1] *Ann. chim. phys.*, [7] **15**, 203 (1898).

[2] *J. Chem. Soc.*, **91**, 1849 (1907).

[3] *Z. anorg. Chem.*, **10**, 189 (1895).

This purified telluric acid was then reduced by hydrazine hydrochloride,[1] by adding a concentrated solution of the latter, in small amounts at a time, to a boiling, concentrated solution of the telluric acid. Reduction takes place readily, the reaction being chiefly that expressed in the equation:

$$2H_2TeO_4 \cdot 2H_2O + 3N_2H_4 \cdot 2HCl = 6HCl + 12H_2O + 2Te + 3N_2$$

The resulting tellurium was collected on a filter, and was washed, first with hot water to free it from hydrochloric acid, and then with alcohol to remove the water. It was then dried at a temperature of 105–110°. Tellurium prepared in this manner varies in color from light gray to black, the tint depending upon the conditions pertaining during the reduction.

The filtrate from the reduction of telluric acid by hydrazine chloride, which contains some of the latter compound together with some tellurium tetrachloride, was utilized for the reduction of further amounts of telluric acid; hydrazine chloride and telluric acid were added to the successive filtrates until the concentration of the hydrochloric acid became so great as seriously to interfere with the further precipitation of tellurium. The tellurium was recovered from this solution of its tetrachloride by evaporating the liquid nearly to dryness to expel the hydrochloric acid, treating the residue with water which hydrolyzes the tellurium tetrachloride, and then reducing the suspended tellurium dioxide by hydrazine chloride.

3. Preparation of Metallic Tellurides.

Since it seemed probable that the most convenient means of preparing large quantities of hydrogen telluride would be afforded by the decomposition of a metallic telluride by water or by an acid, tellurides of certain elements were prepared and the yield of hydrogen telluride from each of them was studied.

In the preliminary experiments the telluride was made by heating proper amounts of tellurium and the metal in question in an atmosphere free from oxygen. The reaction was carried out in a flask that was made by blowing a small bulb on the end of a piece of combustion tubing that was about 25 centimeters long. This flask was supported in a vertical position, and the air in it was displaced by a current of nitrogen that was introduced through a tube reaching nearly to the bottom of the flask. Either all of the mixture of tellurium and the metal that was to be heated was placed in the flask, or, in those cases where the combination of the elements took place with considerable violence, portions of the mixture were dropped into the heated flask from time to time. The flask was heated by the flame of a Bunsen burner to the temperature at which the union of the two elements readily resulted.

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[1] The hydrazine hydrochloride was prepared in large quantities from hydrazine sulfate (Raschig) in the following manner: Hydrazine sulfate was dissolved in hot water and the equivalent amount of barium chloride in solution was added. The liquid was thoroughly stirred by a current of air, and was then allowed to stand until the greater part of the barium sulfate had separated out. A sample of the supernatant liquid was then drawn off and filtered, and this filtrate was tested for barium and for sulfate. A small amount of barium chloride or hydrazine sulfate was added until the final solution contained a very slight excess of barium chloride. The barium sulfate was then allowed to settle out, the supernatant liquid drawn off, filtered, and then evaporated to such point that the hydrazine chloride would crystallize. Recrystallization of this product gave a hydrazine chloride that was free from sulfate and that contained but a very slight trace of barium chloride.

The approximate yield of hydrogen telluride from each sample of metallic telluride prepared in the above manner was determined by decomposing the telluride in the flask in which it had been made. The flask was fitted with a three-hole stopper that carried an inlet tube for the admission of nitrogen, an outlet tube, and a separatory funnel through which the decomposing liquid was introduced. The outlet tube was joined to a chain of apparatus that comprised a test tube containing water, U-tubes containing calcium chloride and phosphorus pentoxide, and finally a test tube containing a solution of cadmium chloride. The telluride was decomposed either by water or by dilute hydrochloric acid. To avoid, so far as possible, the decomposition of the hydrogen telluride during the evaluation of the sample, the water in the test tube next to the flask was first boiled to free it from dissolved oxygen and was cooled by ice and salt during the run; the decomposing liquid, either water or dilute hydrochloric acid, was boiled to free it from dissolved oxygen, and was cooled nearly to 0° before being placed in the separatory funnel; the flask containing the sample of telluride was immersed in a solution of salt that was kept at a temperature of about 10° by surrounding it by a freezing mixture, and the air was completely removed from the apparatus by passing through it a current of nitrogen. After the air in the chain had been displaced, the decomposition of the sample was effected by slowly dropping water, or dilute hydrochloric acid, from the separatory funnel upon the metallic telluride in the flask. The gas that was evolved, which consisted chiefly of hydrogen and hydrogen telluride, passed through the chain of apparatus, was freed from hydrogen chloride by the water in the test tube, was freed from moisture by the calcium chloride and phosphorus pentoxide, and the hydrogen telluride then reacted with the cadmium chloride to form a precipitate of cadmium telluride. The gas was washed and dried before passing it through the solution of cadmium chloride because these operations would be necessary in any subsequent method for the preparation of pure hydrogen telluride, and it was consequently desirable in these preliminary experiments to determine the yield of gas under the conditions that would later pertain. It was noted that the hydrogen telluride was decomposed by the water in the test tube to an extent sufficient to cause the separation of a black, flaky deposit of tellurium. Moreover, the calcium chloride and the phosphorus pentoxide, as well as the walls of the U-tubes that contained these substances, became blackened by tellurium that was set free by the spontaneous decomposition of the gas. It is evident, therefore, that the washing and drying of the hydrogen telluride in the manner above described materially decrease the yield of the gas.

Zinc Telluride.—When a mixture of powdered zinc and powdered tellurium, in equi-atomic proportions, was heated in the flask to dull redness, combination of the two elements took place quietly, the resulting product had a brownish red color, was stable in dry air, and was slowly decomposed by moist air or by dilute hydrochloric acid with the evolution of a mixture of hydrogen and hydrogen telluride in which hydrogen predominated.

Antimony Telluride.—Mixtures of powdered antimony and powdered tellurium in varying proportions melted quietly when the flask was heated, but gave no visible indication of chemical action. When the two substances, in the proportion called for by the formula Sb_2Te_3, were heated together, the product was tin-white in color, stable in the air, and not affected by cold, dilute hydrochloric acid.

Iron Telluride.—When a mixture of powdered iron and powdered tellurium, in equi-atomic proportions, was heated, the reaction took place quietly and a black product, that was not attacked by cold, dilute hydrochloric acid, resulted.

Magnesium Telluride.—Powdered magnesium and powdered tellurium, in equi-atomic proportions, combine vigorously when heat is applied to the mixture, and for this reason this telluride was prepared by successively dropping small amounts of the mixture into the flask. When neither constituent is present in excess, the product is pure white in color. This magnesium telluride is decomposed by moist air with the formation of hydrogen telluride; this, in turn, is acted upon by the oxygen of the air with the liberation of tellurium which forms a black deposit on the surface of the telluride. The compound is rapidly decomposed by water or by dilute hydrochloric acid with the evolution of hydrogen and hydrogen telluride.

Aluminum Telluride.—When a mixture of powdered aluminum and powdered tellurium in the proportion called for by the formula Al_2Te_3 was placed in the flask and the reaction was started by heating the flask to dull redness, the union of the two elements proceeded with almost explosive violence. The product was of a brownish color and was decomposed by moist air more rapidly than was magnesium telluride. When water or dilute hydrochloric acid was brought into contact with the aluminum telluride, there resulted vigorous reaction which was accompanied by the evolution of a large amount of heat and the production of hydrogen and hydrogen telluride.

Of these five metallic tellurides, aluminum telluride gave the highest yield of hydrogen telluride. Calculating the yield on the basis of the tellurium obtained as hydrogen telluride compared to the amount of tellurium employed in the preparation of the metallic telluride, the yield from the aluminum telluride was 10%, a value slightly higher than that obtained for magnesium telluride. In no case did the yield from the latter substance approximate what would be expected from a statement by Berthelot and Fabre[1] to the effect that pure magnesium telluride yields, on decomposition, a gas that is entirely absorbed by potassium hydroxide

4. Preparation of Hydrogen Telluride from Aluminum Telluride.

The preparation of hydrogen telluride from somewhat larger amounts of aluminum telluride was next taken up. The small flask used in the preliminary experiments was replaced by a Kjeldahl flask of Jena glass of 250 cc. capacity. This was placed upright in a clamp, a current of nitrogen was passed into the flask to displace the air, and the bottom of the flask was heated to dull redness by means of a Bunsen flame The mixture of powdered aluminum and tellurium was then dropped into the flask in small amounts at a time, the successive additions to the mixture being made only after the union of the elements in the preceding portion was complete. After a few grams of the telluride had formed, the mass became sufficiently hot to cause subsequent portions of the mixture to react without the application of external heat. When the flask became filled with the product it was carefully stoppered to prevent the entrance of moisture. The operation was then repeated in other flasks until about two kilograms of the aluminum telluride had been prepared The violence of the reaction between aluminum and tellurium, and consequently the amount of the mixture that can be dropped into the flask at a time, depend upon the physical condition of the tellurium, and this varies with the manner of its preparation.

The tellurium and aluminum were first used in the proportion of 3Te . 2Al, but later it was found that a better yield of hydrogen telluride is obtained when a proportionately larger amount of aluminum is used in the preparation of the aluminum telluride. Consequently in the later experiments an excess of about 30% of aluminum above the amount called for in the ratio 3Te : 2Al was employed.

The reaction between aluminum and tellurium is so violent as to cause the expulsion of fine particles of the telluride from the mouth of the flask into the air. These particles readily decompose and form some hydrogen telluride. It is therefore important that the apparatus be placed in a hood with strong draft to protect the operator from the possibility of inhalation of hydrogen telluride.[1]

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[1] *Ann. chim. phys.*, [6] 14, 103 (1888).

Hydrogen telluride was next prepared by decomposing aluminum telluride with dilute hydrochloric acid. The decomposition of large amounts of aluminum telluride by the addition of water or dilute hydrochloric acid to the entire mass gives a very unsatisfactory yield of hydrogen telluride, for the reason that it is difficult to prevent a marked rise in temperature because of the appreciable heat of reaction between aluminum telluride and water. The apparatus that was finally devised to overcome this difficulty is shown in Fig. 1. With its use it is possible to rapidly bring about the interaction of successive small amounts of aluminum telluride and dilute hydrochloric acid in a small, cooled chamber without allowing air to enter the apparatus, or hydrogen telluride to escape into the room.

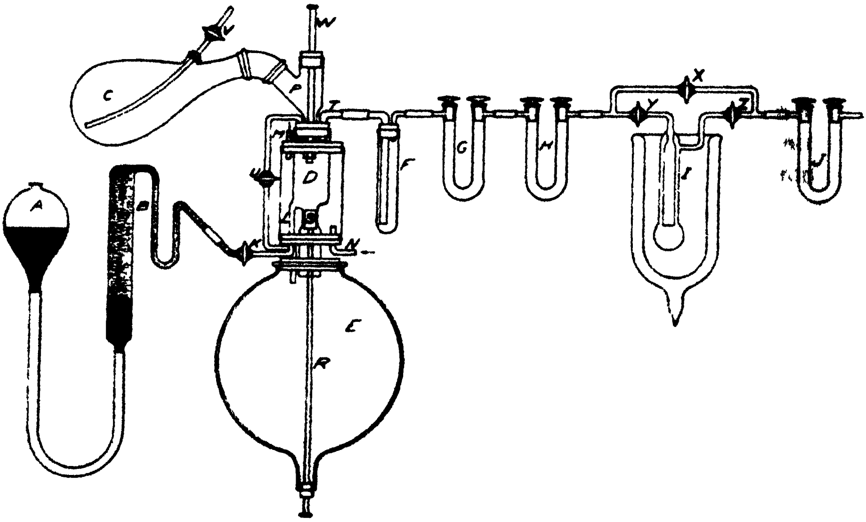

Fig. 1

The aluminum telluride is placed in the flask *C*. It is brought into contact with dilute hydrochloric acid in the chamber *D*, and there decomposed. The slime that is formed in the reaction is drawn off into the flask *E*. The decomposing liquid, dilute hydrochloric acid, is contained in the tube *B* and is driven over into the apparatus by the mercury in the level-bulb *A*. The pear-shaped container *C* is joined with a hopper, *P*, by means of a piece of rubber tubing of large diameter and of a length of about 5 cm. The decomposition chamber *D* is closed at the top by a rubber stopper, through which are inserted the lower end of the hopper *P*, the exit tube *T*, and another tube which joins *D* to *E*. The lower opening of *D* may be closed by a rubber stopper, *S*, which is fastened to the glass rod *R*. When *S* is in the position shown in the figure, it closes the lower end of *D* and supports the aluminum telluride during the decomposition. By drawing the glass rod downward through the rubber stopper in the lower end of *D*, *D* is brought into communication with *E*, and any material that has collected in *D* may be washed down into *E*. The chamber *D* is surrounded by a water jacket with inlet and outlet tubes *MN*. The tube *L* serves as an inlet for the decomposing liquid from *B*, and connection between *L* and *B* is made with a short piece of rubber tubing.

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[1] The inhalation of a small amount of hydrogen telluride causes an inflammation of the throat and nasal passages, and when a larger amount of the gas is inhaled it causes the sensation of an acute inflammation of the lungs.

The gases that are evolved in the reaction pass through a chain of apparatus that comprises. a test tube, *F*, that contains water free from dissolved oxygen, which absorbs any hydrogen chloride that may be carried over from *D*; a U-tube, *G*, that contains calcium chloride and a U-tube, *H*, that contains phosphorus pentoxide, these two tubes serving to dry the gas mixture; a tube, *I*, in which the hydrogen telluride is condensed, and a U-tube, *J*, that contains calcium chloride which serves to prevent the entrance of moisture into the exit tube of *I*. There is also connected to the outlet tube of *J* a wash bottle that contains either nitric acid or a concentrated solution of potassium hydroxide, and which thus serves to prevent the escape of any hydrogen telluride into the room.

The evolution of hydrogen telluride with the aid of the apparatus was carried on as follows: From 300 to 500 g. of aluminum telluride were placed in the flask *C*, and the air in the entire apparatus was displaced by passing nitrogen gas in at *V*, allowing the gas to escape first through the end of the tail stopcock *K*, then through the lower opening of *E*, and finally out of the exit tube of *J*. The tube *B* was filled with dilute hydrochloric acid that had previously been boiled to free it from air. *B* was then connected to *L* and the air in *B* was driven out through the side arm of the tail stopcock *K*. The rod *R* was then pushed up until the stopper *S* closed the lower opening of *D*.

A few grams of aluminum telluride were now introduced into *D* through the side arm of *P* by raising the container *C*. The dilute hydrochloric acid in *D* was then slowly run into *C* through the stopcock *K*, the liquid in *B* being kept under a pressure somewhat above that of the atmosphere by raising the level-bulb *A* which is filled with mercury. Gas was rapidly evolved in *D* and passed from it through the chain of apparatus. After the decomposition of this portion of aluminum telluride was complete, the rod *R* was lowered, and the contents of *D*, consisting of aluminum hydroxide, aluminum chloride and tellurium, was washed down into *E* by means of more of the acid from *B*. The stopper *S* was then again pushed up into place and the operation was repeated until all of the aluminum telluride in *C* had been decomposed. Throughout these several operations the reaction chamber *D* was surrounded by a cold, circulating salt solution to lessen, so far as possible, the decomposition of hydrogen telluride by the heat produced in the reaction. Pieces of aluminum telluride stuck at times in the inlet tube below *P* and the glass rod plunger *W* served to displace these and push them down into the decomposition chamber. There was a slow evolution of gas, chiefly hydrogen, from the material that had been washed down into *E*, and the gas pressure that was thus caused was relieved, from time to time, by opening the stopcock *U* when the lower opening of *D* was closed by the plug *S*. The exit tube *T* was of rather large diameter to prevent its being clogged by the tellurium and aluminum hydroxide that are carried over by the foaming of the material during the reaction.

The hydrogen telluride that was formed in this manner was condensed in the tube *I* which was immersed in liquid air during the decomposition of the aluminum telluride.

The yield of hydrogen telluride from the decomposition of from 300 to 500 g. of aluminum telluride in this apparatus was found to vary from 2 to 5%, which is much lower than the yield that was obtained with small portions of the material. Moreover, it was found that the gas evolved from the aluminum telluride did not consist entirely of hydrogen and hydrogen telluride. In some of the early experiments white fumes were seen to issue from the exit tube of the decomposition flask (see Part 5). It seemed possible that these fumes might be due to the formation of silicon dioxide from the decomposition of silicon hydride in the gas mixture. To ascertain whether this supposition was correct, about one-fifth of the hydrogen telluride from one of the runs was distilled off, and passed into a dilute solution of potassium hydroxide, which would react with any silicon hydride that might be present to form potassium silicate. The potassium telluride that was formed in the absorbing liquid was decomposed by blowing air through the solution which was then filtered, acidified with hydrochloric acid, and refiltered to remove the small amount of tellurium that separated. The filtrate was then evaporated to dryness. The residue was treated with water to remove potassium chloride, and the silica was collected on an ashless filter, and was dried, ignited, and weighed. A blank determination was also made by acidifying a solution containing the same amount of potassium hydroxide as was used above, and evaporating to dryness. The results were as follows:

	Experiment.	Blank.
Weight crucible + silica	12.1297	12.0837
Weight crucible	12.0997	12.0712
Weight silica	0.0300	0.0125

Weight silica from SiH_4 = 0.0300 — 0.0125 = 0.0175 gram.

It is apparent, therefore, that when the gas is prepared in the manner here described an appreciable amount of silicon hydride is present in the hydrogen telluride. This, probably, is due to the presence of aluminum silicide, the silicon either being present in the aluminum, or being extracted from the glass of the decomposition flask when the telluride is prepared. In the determinations that were made after the presence of silicon hydride in the evolved gas had been detected, the hydrogen telluride was freed, so far as possible, from silicon hydride by passing a current of nitrogen over the liquefied gases at a temperature slightly below the boiling point of hydrogen telluride.

5. Fractional Distillation of Hydrogen Telluride Prepared from Aluminum Telluride.

The hydrogen telluride that had been collected in *I*, Fig. 1, was decomposed by passing it through small flasks of the form shown in Fig 2, these flasks being made from Jena glass tubing of a diameter approximately 1.8 cm. The inlet tube is also of Jena glass, and is ground into the neck of the flask. The flasks were heated in small electric resistance furnaces to 500°. At this temperature the decomposition of hydrogen telluride into tellurium and hydrogen seems to take place most readily,[1] and the resulting tellurium melts and flows together in a globule in which form it may conveniently be weighed.

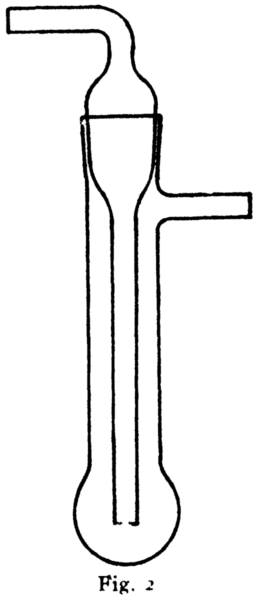

Fig. 2

The decomposition of the hydrogen telluride was carried out in the following manner: The stopcocks *Y* and *Z* of the tube *I* were closed and the tube was disconnected from the chain of apparatus. One end of *I* was then joined directly to the inlet tube of one of the decomposition flasks by means of a small piece of rubber tubing, the ends of the glass tubes being brought into contact within the rubber. A current of dry nitrogen was then passed into the other end of *I* and through the upper tube *X*, the stopcock of which was open. While the air in the flask was being displaced by the nitrogen, the electric furnace was brought up into position around the flask, and the flask heated to 500° When all air had been removed from the apparatus, the stopcocks *Y* and *Z* were opened, *X* was closed, and nitrogen was slowly passed over the frozen hydrogen telluride and through the flask.

The Dewar tube containing the liquid air was then lowered to such a distance as to cause the hydrogen telluride in *I* to melt and slowly vaporize. After tellurium sufficient in amount for one fraction had been collected in the flask, the stopcock *Z* was closed and the liquid air under *I* was raised at such speed that the increase of pressure due to the inflowing nitrogen was counterbalanced by the decrease of pressure caused by the cooling of the apparatus. When the bulb of the flask had been entirely immersed in liquid air and the pressure on the inside of the flask had begun to rise, the stopcock *Y* was closed, the stopcock *X* opened, and nitrogen was again allowed to pass through the flask. Any hydrogen telluride still remaining in the connecting tubes was thus quickly driven over into the flask and decomposed, whereupon the furnace was removed and the flask containing the globule of tellurium was allowed to cool to room temperature. While this was taking place, the current of nitrogen was maintained at a speed sufficient to prevent air from being drawn back into the flask as the latter cooled. When the flask had reached room temperature it was replaced by a second flask, and the operation was repeated until all of the hydrogen telluride that had been collected in *I* had been decomposed. It was possible in this manner to decompose successive portions of hydrogen telluride, and to collect the globules of metallic tellurium without allowing air at any time to come in contact either with the gas or with the tellurium while the latter was hot enough to cause it to unite with the oxygen of the air.

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[1] Ditte, *Annales Scientifiques de l'École Normale,* [2] I, 293 (1872).

6. The Atomic Weight of Tellurium Prepared from Aluminum Telluride.

The atomic weight of the tellurium comprising the several fractions that were made in the manner just described was determined by dissolving the globule of tellurium in nitric acid, evaporating the solution to dryness and heating the residue until all nitric acid had been driven off and any basic nitrate present had been decomposed. The atomic weight of the sample was then calculated from the ratio of tellurium to tellurium dioxide.

All of the operations—the solution of the tellurium, evaporation and subsequent heating of the residue—were performed in a single flask, Fig. 3, without the removal of the material. The flask was blown from Jena combustion tubing and the float *A* was also made of Jena glass. The relative sizes of the float and the opening of the constriction in the flask are shown in the figure. Two protuberances were blown out just above the constriction to allow space for the float when that occupied a horizontal position.

The flask and the float were first carefully cleaned, dried and weighed. A globule of tellurium was then placed in the flask, the piece being of such size that it would drop through the constriction. The apparatus was weighed once more to obtain the weight of the tellurium. Nitric acid

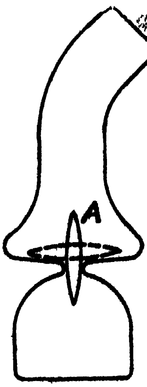

Fig. 3.

of 1.25 specific gravity was then poured into the flask until the lower bulb was half filled, and by gently shaking the flask, the float *A* was brought into a vertical position in the constriction and about 3 cm. of distilled water were then poured into the flask. The reaction between the tellurium and the nitric acid is in the beginning so slow as to allow ample time to adjust the float and add the distilled water before any spattering occurs. All of the nitric oxide that is evolved must bubble through the water in the upper compartment, and this serves effectually to prevent mechanical loss of tellurium dioxide during solution. When the tellurium had completely dissolved, the flask and its contents were cooled, whereupon the water flowed into the lower compartment. The float was then brought into horizontal position by gently shaking the flask, and the contents of the apparatus were evaporated to dryness in one of the electric furnaces previously mentioned. The float was then again brought into vertical position to prevent mechanical loss of tellurium dioxide during the next operation, and the temperature of the furnace was raised to 650° at a rate of about 100° per hour. At this higher temperature any basic tellurium nitrate is decomposed into the dioxide and the tellurium dioxide is fused. For convenience in regulating the temperatures during these operations the electric furnaces were first calibrated, amperes being plotted against temperatures.

At the end of the heating, the flask was cooled, and was then weighed, the increase in weight being equal to the weight of the oxygen that had combined with the tellurium. All weighings were made by the method of vibrations with calibrated weights, and the flasks were allowed to stand in the balance case for several hours before weighing.

Several runs were made with the apparatus described under Part 4. The resulting hydrogen telluride was fractionally decomposed, and the atomic weight of the tellurium in each of the several fractions was determined. Forty-five determinations, representing the total number of fractions from the decomposition of the hydrogen telluride obtained in eleven runs, were made. Of these determinations thirty-one gave values between 127.3 and 127.8, the average being 127.6. Sixteen of the determinations gave values between 127.5 and 127.7 with an average of 127.61 for the atomic weight of tellurium. It is clear, therefore, that the method does not give closely agreeing results. This lack of accuracy appears to be due, first, to the large size of the flask and the consequent variation in the amounts of moisture that would condense on its surface and affect the weighings, and, second, to the unsatisfactory character of the ratio Te : TeO_2 for the determination of the atomic weight of tellurium. The difference between the weight of the tellurium that was used and of the tellurium dioxide that was formed from it is relatively so small as to necessitate the employment of large samples if accurate results are to be obtained. In the determinations that were here made, the globules of tellurium ranged from 0.4 to 0.8 g. in weight. With a sample weighing 0.6 g., an error of one-tenth of a milligram in its weight would cause an error of eight-hundredths of a unit in the atomic weight of tellurium. Globules of greater size could not be used without increasing the size of the flask, and this, for the reasons given above, would not have enhanced the accuracy of the determinations. It seems evident, therefore, that this method for the determination of the atomic weight of tellurium does not, under the conditions above described, yield accurate results. The yield of hydrogen telluride from aluminum telluride was, moreover, so small as to necessitate the development of a more satisfactory method for the preparation of hydrogen telluride if the fractional distillation of the gas were to be carried out on a scale sufficiently large to yield conclusive results.

7. Preparation of Hydrogen Telluride by Electrolysis.

Ernyei[1] discovered that hydrogen telluride is formed when dilute sulfuric acid is electrolyzed with a tellurium cathode. This method was examined to ascertain whether it might not be utilized in the preparation of large quantities of the pure gas. It seemed advisable, however, to use an electrolyte other than sulfuric acid because of the possibility of the formation of volatile compounds of sulfur, the analogue of tellurium.

Preliminary experiments with an apparatus similar to that of Hofmann for the electrolysis of hydrochloric acid showed that hydrogen telluride that is free from volatile compounds of phosphorus is formed when the electrolysis is carried on with a tellurium cathode, a platinum anode, and a 50% solution of orthophosphoric acid as the electrolyte. It was also ascertained that the best yield resulted when the temperature of the electrolyte was kept at 0°. At higher temperatures some of the hydrogen telluride would be decomposed; a lower temperature than 0° would be of no advantage because the hydrogen telluride would be liquefied, and would remain in the apparatus until the temperature was allowed to rise above 0°. The run at 0° gave the following efficiencies:

$$\frac{100\ \mathrm{H}}{\mathrm{T}} = 22\%,\ \frac{100\ \mathrm{L}}{\mathrm{T}} = 27\%,\ \text{and}\ \frac{100\ \mathrm{H}}{\mathrm{L}} = 82\%$$

in which H represents the weight of the tellurium in the hydrogen telluride that was formed; T, the theoretical cathode loss, figured from the amperage and the duration of the run; and L, the actual cathode loss, ascertained from the weight of the cathode before and after the run. The weight of hydrogen telluride that was formed was determined by passing the gas into a solution of cadmium chloride, and weighing the resulting cadmium telluride. The preliminary experiments also show that for the continuous production of hydrogen telluride over a period of several hours, the following factors are of importance:

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[1] *Z. anorg. Chem.*, 25, 313 (1900)

(*a*) Minimum distance between the electrodes. The resistance of the electrolyte, and consequently the heating effect of the current, is lessened by decreasing the distance between the electrodes.

(*b*) Minimum space above the electrolyte in the cathode compartments. Small free space above the electrolyte shortens the time between the evolution of the gas and its condensation, and thus decreases the loss of hydrogen telluride by spontaneous decomposition.

It further is advantageous to lessen the diffusion of oxygen from the anode into the cathode compartment so far as possible, and to employ low current density because that favors high reduction efficiency.

With these points in mind, the cell for the production of hydrogen telluride was constructed as shown in Fig. 4.

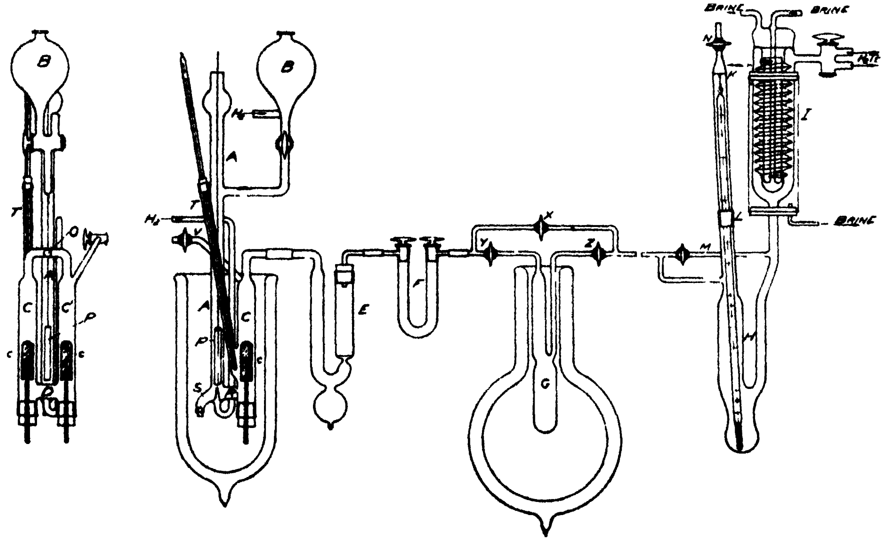

Fig. 4.

Description of Apparatus.—Two views, one from the front and one from the side, of the apparatus in which the electrolysis was carried on, are shown in the figure. The two cathode tubes *C* and *C'* were about 2 cm. in diameter, and were joined together at the top. They had a common outlet *O* through which the hydrogen telluride passed on into the tube *E*. They were furthermore joined together near the bottom by the tube *D* which was 2.5 cm. long. The anode tube *A* was connected to *D* by a short tube, *R*. The tellurium cathodes *c* and *c'* weighed about 50 g. each and were about 1.3 cm. in diameter. They were prepared by fusing tellurium in hard glass tubes that were sealed at one end, inserting a platinum rod in the molten tellurium and holding it in place until the metal solidified. The glass tube was then carefully broken off with a hammer. These tellurium cathodes were held in upright position by forcing the ends of the platinum rods into holes drilled in brass rods, the rods being inserted in one-hole rubber stoppers. In the drawing, the brass rods are represented by the heavy black lines. Those portions of the platinum rods between the tellurium and the brass were encased in glass tubes which were slipped over the platinum rods before the latter were inserted into the brass holders. These protecting glass tubes were pushed into the opening in the rubber stoppers for a short distance. The cathodes were adjusted at such height as to bring their lower ends just above the opening into the anode tube, so as to keep the distance from anode to cathode as small as possible. The stoppers supporting the cathodes reached nearly to the lower side of the tube *D*. This served to prevent the pocketing above each stopper of some of the electrolyte which might be frozen on the application of external refrigerant and thus damage the apparatus.

At the proper height on one of the cathode tubes (*C* in the figure) was attached a side arm, *T*, through which a thermometer was inserted, the bulb of the thermometer being brought nearly in contact with the electrode. This arrangement permitted of accurate control of the temperature within the cell, and it was preferable to the insertion of the thermometer from directly above the electrode through the upper end of one of the cathode tubes: first, because the space above the electrolyte in the cathode tube could thus be made smaller than if the tube were large enough to accommodate the thermometer bulb and the electrode side by side,[1] and, second, it avoided the decomposing action upon the hydrogen telluride of the stopper that must have been used to hold the thermometer in place. If the thermometer had been placed entirely within the apparatus it would have been impossible to read it because the hydrogen telluride was found to decompose and to deposit a mirror-like layer of tellurium on the inner walls of the tube. The zero point on the toluene thermometer that was used was near the upper end of the thermometer, and was consequently above the rubber stopper that held the thermometer in place.

The anode *P* consisted of a small roll of sheet platinum, and was suspended by a platinum wire in the anode tube at such height that its lower end was but slightly above the opening in the side arm. The glass tip, shown in the figure just at the left of *R*, served as the inlet of a current of hydrogen, which was caused to bubble up through the liquid in the anode tube during electrolysis to prevent, so far as possible, solution of the oxygen that is evolved in the electrolyte. The side arm *S*, which could be closed with a small cork, served to draw off the electrolyte when the apparatus was cleaned, or when the electrolyte was to be renewed.

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[1] The measurement of temperature would not have been accurate if the thermometer had been placed above the electrode.

The side arm, attached to the upper part of the anode tube *A*, carried a two-way stopcock and the bulb *B*. By turning the stopcock into suitable position, the electrolyte could be introduced into the apparatus from *B*, and by turning the stopcock through 180°, hydrogen could be passed through it into the apparatus to free the latter from air. A side arm, *V*, attached to the cathode tube *C'*, served as an inlet for hydrogen when that gas was passed through the chain of apparatus, after a run, to drive the hydrogen telluride over into the condensing tube.

Manipulation of Apparatus.—With the apparatus set up as shown in Fig. 4, with the exception that the anode was not yet inserted, the preparation of hydrogen telluride was carried on as follows:

A current of hydrogen was admitted through the side arm of the stopcock below *B* and was passed through the chain of apparatus until the air was completely displaced. While this was being done a cork was inserted in the top of the anode tube *A* to prevent the escape of hydrogen in that direction. When all air had been removed, the stopcock below *B* was turned, and the 50% solution of orthophosphoric acid, that had been boiled to free it from dissolved oxygen, was run in until the liquid stood about 1 cm. above the top of the tellurium cathodes. The cork in the upper end of the anode tube was then removed and the platinum anode was placed in position. The anode and the two cathodes were then connected to the source of current. There was then brought up around the apparatus a large Dewar tube that was filled with a mixture of solid carbon dioxide and alcohol. When the temperature in the apparatus had fallen to 0° a direct current at 110 volts was turned on. The temperature in the cell was kept near 0° by the addition, from time to time, of solid carbon dioxide. It was found that, with no external resistance in the circuit, a current of about five amperes flowed through the cell, and this was found to be too high to permit of thorough cooling by the refrigerant. The current was consequently cut down to about four amperes and maintained at that value. Under these conditions the temperature of the cell could easily be maintained at 0° by the addition of suitable amounts of carbon dioxide. A current of hydrogen was bubbled through the anode liquid throughout the electrolysis.

The gases from the cathode, hydrogen and hydrogen telluride, rose in the cathode tubes *C* and *C'* and passed over into the U-tube *E* which served to catch any phosphoric acid or tellurium that might be carried over by the foaming of the electrolyte. The further arm of the tube *E* was filled with calcium chloride, which served to free the gases from some of the moisture that they contained. An opening in the lower bulb of *E*, which was kept closed during the run by a stopper, made it possible to draw off from the U-tube, between the runs, any liquid material that had collected in the tube. The U-tube *F* was charged with phosphorus pentoxide, which served to complete the drying of the gases. The hydrogen telluride was condensed in the receptacle *G*. The exit tube beyond the stopcock *Z* was connected to two U-tubes that are not shown in the figure, one of these tubes containing calcium chloride to prevent the back diffusion of moisture into *G*, and the second tube containing nitric acid, which would decompose any hydrogen telluride that might pass over from *G*, and thus prevent the escape of that gas into the room. The condensation of the hydrogen telluride in *G* was effected by bringing up around *G* a Dewar bulb containing liquid air.

The apparatus was run continuously for three to six hours at a time. At the end of each run hydrogen was passed in at *V* until the hydrogen telluride had been completely driven over into *G* and there condensed. The stopcocks on *F* and *G* were then closed and the cell and the U-tube *E* were detached, cleaned, and then reconnected to the apparatus for the next run. The manipulation above described was then repeated; but *Y* and *Z* were not opened at the beginning of a run until the air in the apparatus had been driven out through the tube *X* and the electrolysis had been started.

The hydrogen telluride produced during each electrolysis was condensed in *G* until there had collected in all about 40 g. of the substance. The duration of the electrolysis was 35 hours; the average current was four amperes. The efficiencies of the entire run were as follows.

$$\frac{100\ \mathrm{H}}{\mathrm{T}} = 12\%, \quad \frac{100\ \mathrm{L}}{\mathrm{T}} = 28\%, \text{ and } \frac{100\ \mathrm{H}}{\mathrm{L}} = 43\%$$

That this run gave a lower yield than the 82% that was obtained in one of the preliminary experiments is probably due to the difficulty in keeping the electrolyte free from oxygen. The ratio of actual to theoretical cathode loss is nearly the same in both cases.

The production of so large an amount of hydrogen telluride as 40 g., by means of successive electrolyses, rendered it necessary to keep the compound constantly frozen in *G* during several days and nights. It was found that, by inserting some wool in the mouth of the Dewar flask, which had a capacity of three liters, a temperature of —110° C. was obtained in the neck of the flask, and this was sufficiently low to effect the condensation and retention of the hydrogen telluride. The Dewar flask itself stood in a felt holder, and two liters of liquid air were found sufficient to maintain the hydrogen telluride in *G* in a frozen condition for two days, or even longer. Hydrogen telluride always condensed in the upper portion of the inlet arm of *G* during a run and thus clogged the tube. When this occurred the Dewar flask was lowered, whereupon the solid hydrogen telluride melted and flowed downward into the cylindrical container at the bottom of the tube.[1]

[1] It may be proper to add that the preparation of hydrogen telluride by the method

8. Fractional Distillation and Decomposition of Hydrogen Telluride.

The hydrogen telluride that had been prepared and condensed in the tube *G*, in the manner above described, was then subjected to fractional distillation with the aid of the apparatus shown in the right-hand portion of Fig. 4. This consisted of a tube, H, similar in form to *G*, which was provided with a thermometer for the determination of the melting and boiling points of the gas; and of a condenser, *I*, for the fractional distillation of the liquid hydrogen telluride. A Friedrichs spiral condenser was adapted to the purpose in hand by attaching a two-way stopcock to the exit tube, and fitting the condenser with a jacket to permit of external cooling. The thermometer was held in place without the aid of a rubber stopper, by suspending it by means of a platinum wire from a thread of glass, *K*, fused across a glass tube and connecting this enclosing tube to the upper end of *H* by a ground glass joint, *L*. A stopcock, *N*, attached to the upper end of the tube, served for the admission of hydrogen.

The tube *M*, connecting the inlet and outlet tubes of *H*, served as a safety device in distilling the hydrogen telluride from *G* into *H*, in case the inlet tube of *H* became clogged by the frozen gas. Before beginning the distillation of the hydrogen telluride the stopcocks *X*, *Y* and *Z* were closed, the apparatus to the left of *Y* was detached and the exit tube beyond *Z* was fused to the inlet tube of *H*. After this had been done, a current of hydrogen was passed through *X* until the air in *H* and *I* had been driven out. In the meantime, a current of brine, cooled to —5° by a mixture of calcium chloride and ice, was passed through the inner and outer condensers of *I*, and the two branches of the exit stopcock at the top of *I* were connected with Kjeldahl flasks that contained redistilled nitric acid of 1.25 specific gravity. This was prepared by diluting redistilled nitric acid with redistilled water. The exit tube of each flask was joined to another Kjeldahl flask containing nitric acid, which served to retain any hydrogen telluride that might pass through the acid in the first flask.

Stopcock *Z* was now opened, *X* was closed and the hydrogen telluride was distilled over into *H*, by lowering the Dewar bulb from around *G* and immersing *H* in a mixture of solid carbon dioxide and alcohol. After the distillation was finished, determinations were made in *H* of the melting and boiling points of hydrogen telluride. The results of these determinations are given on a later page. The refrigerant around *H* was then removed and the liquid was allowed to vaporize slowly. The gas that escaped condensation in *I* passed over through one of the exit tubes of the stopcock into nitric acid, and was there oxidized to tellurium dioxide.

here described was completed in January, 1911, some time before the appearance of the article by Hempel and Weber [*Z. anorg. Chem.*, 77, 48 (1912)], in which a modification of Ernyei's procedure was described.

When sufficient of this substance had collected in the first flask, the stopcock was turned through 180°, and the gas was passed into the flask attached to the other arm, the first flask being in the meantime replaced by a third flask. This process was continued until the entire quantity of hydrogen telluride had been fractionally distilled and decomposed. The solutions of tellurium dioxide and nitric acid that were thus obtained were evaporated to dryness in the Kjeldahl flasks and the residues, which consisted of tellurium dioxide and basic tellurium nitrate, were transferred to porcelain crucibles and were fused therein to effect the complete removal of nitric acid.

9. Determination of the Atomic Weight of Tellurium.

Lenher[1] determined the atomic weight of tellurium by decomposing weighed amounts of the double salt K_2TeBr_6 by means of chlorine and hydrogen chloride, and weighing the potassium chloride that was formed. The apparent simplicity of this method and the close agreement of the results that were obtained by Lenher through its use led the authors to attempt to employ it. It was found, however, to be impossible completely to free the potassium tellurium bromide from water without causing decomposition of the salt. Lenher states that he removed the last traces of moisture and hydrogen bromide from the compound by letting it stand over soda lime for eight months. Attempts were made to dehydrate the double salt and remove the hydrogen bromide by placing potassium tellurium bromide, that had been carefully recrystallized and centrifuged after each crystallization, in a vacuum desiccator over phosphorus pentoxide and fused potassium hydroxide. In some experiments the salt was allowed to stand at the temperature of the room, and in others it was raised to different temperatures (from 80° to 150°) by means of an electric "hot-plate" within the desiccator, but in no case was it found possible to completely dry the salt without decomposing it to some extent.

Inasmuch as accurate *comparative* determinations of the atomic weight of tellurium in the several fractions would serve the object of the present research quite as well as absolute determinations of the atomic weight of the element, the volumetric method suggested by Brauner[2] and modified by Gooch and Danner[3] was examined and was finally adopted. It was carried out by the authors in the following manner: Weighed amounts (usually about 0.5 g.) of tellurium dioxide were dissolved in an approximately 10% solution of potassium hydroxide and about 25 cc. of sulfuric acid (1 : 1) were added. The solution was heated to about 60°, and an excess of a standardized $N/20$ solution of potassium permanganate slowly added. The oxidation of the tellurium dioxide does not take place very rapidly, and it is accompanied by precipitation of some manganese dioxide. An excess of a standardized solution of ammonium oxalate, of about the same strength as the potassium permanganate, was now added, and the solution was reheated to 60° and was kept at that temperature until the precipitate disappeared. The titration was then completed with the solution of potassium permanganate. The computation of results is based upon the reaction expressed by the equation

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[1] THIS JOURNAL, 31, 20 (1909).

[2] *Chem. News*, 63, 136 (1891).

[3] *Am. J. Sci.*, 144, 301 (1892). See also Morgan, *Loc. cit.*

$$5TeO_2 + 2KMnO_4 + 3H_2SO_4 = 5TeO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

To ascertain whether the method would yield concordant results, preliminary experiments were made on fused tellurium dioxide that was obtained by heating purified telluric acid prepared as described in Part 2. Five determinations on different portions of the same material gave results for the atomic weight of tellurium that agreed within 0.12 of a unit. The method was then employed for the determination of the atomic weight of the tellurium in the various fractions prepared as already described, and the results that were obtained are set forth in Table I.

TABLE I.

Fraction		Atomic weight.	
1		127.52	127.41
2		127.49	127.41
3		127.46	127.45
4		127.43	127.52
5		127.36	127.46
6		127.50	127.51
7		127.59	127.51
8		127.57	127.57
9		127.76	.
10		127.40	127.42
11		127.74	.
12		127.45	127.41
13		127.38	127.43
14		127.41	127.40
15		127.56	127.47
16		127.52	127.54
17		127.44	127.47
Average		127.50	127.47
a	129.35	129.05	127.69
b	129.85	129.08	127.62
c	128.24	127.81	127.48
y	128.06	..	127.52
z	127.72	..	..

Fractions 9 and 11.—The first two determinations on Fraction 9, and on Fraction 11 also, gave low results, about 127.0 for each. The tellurium in each of the solutions that remained after the titrations of these fractions was then recovered and purified. Sulfuric acid was first removed by the addition of an excess of barium chloride, the supernatant liquid decanted and evaporated to a volume of about 150 cc., and the tellurium was precipitated therefrom by an excess of hydrazine chloride. This tellurium was washed until free from chlorides, dissolved in hydrochloric acid, to which a little nitric acid was added, and the resulting tellurium tetrachloride was hydrolyzed with water, complete precipitation of the dioxide being effected by adding ammonium hydroxide to slight alkaline reaction, and then acetic acid to slight acid reaction. This material (TeO_2) was washed by decantation, dissolved in hydrochloric acid, and again precipitated as above. After a repetition of this process, the tellurium dioxide was finally dried and fused. Each fraction was then again titrated with potassium permanganate, and the results that were obtained are those given in the table.

Fraction a.—Some hydrogen telluride escaped condensation during the preparation of the hydrogen telluride, and it was caught in a wash-bottle containing nitric acid. A further amount of hydrogen telluride passed over into this wash bottle whenever the solidified hydrogen telluride was melted to clear the inlet tube of *G*, Fig. 4. The first determination of the atomic weight of the tellurium that collected in this wash bottle yielded a result of 129.35. The tellurium dioxide was then dissolved in nitric acid, the solution filtered, evaporated to dryness, and the product was fused. A result of 129.05 was then obtained. This material was then purified by the method outlined under "Fractions 9 and 11," and a result of 127.69 was obtained.

Fraction b.—On distilling the hydrogen telluride from tube *G* into the tube *H*, a small amount escaped condensation and passed over into nitric acid by which it was decomposed. The first titration of this material gave an atomic weight of 129.85. It was then hydrolyzed twice in the manner described under "Fractions 9 and 11," and the redetermination of the atomic weight gave 129.08. The tellurium was next recovered from all of the various titrations of Fraction *a* and was purified by the process used on Fractions 9 and 11. The resulting material gave 127.62.

Fraction c.—During the determinations of the melting and boiling points of the hydrogen telluride, some of the gas escaped and was decomposed by nitric acid. The value that was obtained from this material was 128.24. Continued fusion of this material brought the result to 127.81. After recovery and purification (see Fractions 9 and 11), 127.48 was obtained as the atomic weight.

Fraction y.—Some tellurium remained in the apparatus after the hydrogen telluride had been completely decomposed. This material showed an atomic weight of tellurium of 128.13 and 127.98, an average of 128.06. After purification similar to that used for Fractions 9 and 11, it showed an atomic weight of 127.52.

Fraction z.—The tellurium which became detached from the cathode during the electrolysis, but which was not converted into hydrogen telluride, was removed from the electrolyte by filtration, purified by the Staudenmaier method and converted into tellurium dioxide. This material gave an atomic weight for tellurium of 127.72.

Discussion of Results.—If the high atomic weight of tellurium is due to the presence of a group analogue of still higher atomic weight, that substance should form a hydrogen compound similar to hydrogen telluride. The hydride of the hypothetical element might be expected, under the experimental conditions herein described, to cause a gradation in the atomic weights of the various fractions, because this substance would probably have a higher boiling point than that of hydrogen telluride, and would consequently tend to concentrate in the later fractions. The earlier fractions would then yield low atomic weights and the later fractions would give higher results. Moreover, low atomic weights would also be obtained with the material from Fractions *a*, *b* and *c*, since these comprise the most volatile portion of the liquefied hydrogen telluride. Fraction *y* would presumably show a high atomic weight because hydrogen telluride would probably be more stable than the hydrogen compound of the hypothetical analogue of tellurium.

If, however, it is assumed that the hydride of the higher analogue of tellurium is not formed under the conditions that pertain in the experiments that have here been described, there would be no gradation in the values for the atomic weights of the various fractions, but the results should be uniformly lower than the atomic weight now accepted for tellurium. The hypothetical analogue would be concentrated in Fraction *z*, and that material should therefore give a higher atomic weight than any of the other fractions.

The results that are given in Table I do not appear to support either of these hypotheses. Fractions 1 to 17 show no gradation in values, nor is the atomic weight of the tellurium in those fractions lower than that obtained with pure tellurium dioxide from other sources. Fractions *a*, *b* and *c* did not yield low results, and the high values that were first obtained were reduced to the now accepted value by purification of the material. Fraction *z* showed an atomic weight that was not materially higher than that obtained with the other fractions, while Fraction *y*, which first showed a high atomic weight, gave a normal value after purification. The high results that were first obtained with Fractions *a*, *b*, *c*, and *y* must be ascribed to the presence of impurities, but the amount of foreign substance in the several samples that were titrated was in each case so small as to practically preclude the possibility of its identification. It is obvious that, since the purification of the material in these several fractions affected all of them alike, it cannot be claimed that the high results first obtained support either of the hypotheses that have been suggested.

It might be urged that the high results first yielded by Fractions *a*, *b*, and *c*, 129.85 to 128.24, indicate that the fractional distillation of hydrogen telluride does actually segregate in certain fractions an element of higher atomic weight than that of tellurium, and that the high values for these fractions are brought down to the now accepted atomic weight because the process of purification of the fractions serves to separate this new substance from the "old" tellurium. To this it may be replied that the methods that were used in the purification of the fractions are not new, and that if they here serve to separate tellurium from an element of higher atomic weight, they would have done so in the hands of other investigators.

The results that are here presented appear, therefore, strongly to indicate that the hypothetical element, dvi-tellurium, does not exist. If this be true, it follows either that the substance now termed tellurium is an element of anomalously high atomic weight, or that which we now term tellurium is a mixture of a "true" tellurium of normal atomic weight with another substance, or perhaps other substances, of slightly higher atomic weight, and of closely similar chemical and physical properties.

Yet this suggestion is open to the criticism that if such were the case the element of higher atomic weight must then be placed beyond iodine in the Periodic Table, and would thus be forced into a group of elements that it does not at all resemble. It is true that the Periodic Table contains pairs of elements, such as nickel and cobalt, praseodymium and neodymium, that differ but little in atomic weight, and closely resemble each other in their properties and in the properties of their compounds. Yet the elements in these pairs are adjacent to each other; they are not separated by elements of distinctly different characteristics.

If the high atomic weight of tellurium is not to be explained by the presence either of a group analogue, dvi-tellurium, of much higher atomic weight, or of an element of but slightly higher atomic weight and of closely similar properties, the inevitable conclusion would seem to be that suggested by Kusnezow and by Werner, who hold that tellurium is not complex and that the atomic weight now assigned to tellurium, 127.5, although abnormal, and greater than that of iodine, is nevertheless the correct value.

10. Properties of Hydrogen Telluride.

(*a*) *The Solvent Action of Hydrogen Telluride upon Tellurium.*—When solidified hydrogen telluride, that has been prepared in an atmosphere free from oxygen, is liquefied by allowing the temperature to rise very gradually to the melting point of the compound, there is obtained a liquid that is either colorless or of a very faint straw-yellow tint. If the temperature is allowed to rise above the melting point, or if a trace of oxygen is admitted to the apparatus, the liquid gradually takes on a deep red color and finally becomes opaque. Observations that were made during the distillation of hydrogen telluride (see Part 8) appear to afford an explanation of these changes in color. At the beginning of the distillation the hydrogen telluride in *G* (Fig. 4) was of a pale yellow color. During the progress of the distillation this color gradually increased in depth, and when the distillation was about half completed, the hydrogen telluride in the tube appeared as a dark red, transparent liquid. At this point, clogging of the inlet tube of *H* by solid hydrogen telluride necessitated the stopping of the distillation, which was done by immersing *G* in liquid air. The entrance of outside air into the apparatus during this operation was prevented in the manner described in Part 5. The inlet tube of *H* was then cleared by lowering the refrigerating mixture, alcohol and carbon dioxide, in which the tube was immersed, and allowing the tube to rise in temperature until the solid hydrogen telluride had melted. When the distillation was resumed, it was noticed that the hydrogen telluride in *G* had become black and opaque, and after the completion of the distillation, a thin layer of black, finely divided tellurium was found upon the inner walls of the lower part of the condensing tube *G*. When the hydrogen telluride that had been condensed in *H* was first melted, it possessed a very pale yellow color that was about the same as that of the liquefied hydrogen telluride in *G* at the beginning of the distillation.

Freshly distilled hydrogen telluride is much lighter in color than the liquefied gas that has stood for some time. When liquefied hydrogen telluride is brought under conditions that favor its decomposition, the depth of its color increases. When liquefied hydrogen telluride of pronounced color is frozen, free tellurium is deposited. These observations would seem to indicate that the color of liquefied hydrogen telluride is due to the solution in the liquid of tellurium that has resulted from the decomposition of the compound. When the conditions are such as would tend to prevent the breaking down of hydrogen telluride, the liquefied gas is almost free from color. It is, therefore, probable that pure liquefied hydrogen telluride is colorless.

(*b*) *Melting Point and Boiling Point of Hydrogen Telluride.*—The melting point and the boiling point of hydrogen telluride have been determined by earlier investigators, but since the redetermination of these values could easily be made in connection with the distillation of the compound, it seemed desirable to repeat the measurements. In many determinations of the melting point of hydrogen telluride, it was found that, although the compound uniformly began to melt at —57°, the temperature did not remain constant throughout the melting of the entire mass, but gradually rose. Liquefied hydrogen telluride was found to begin to boil at 0°, but the temperature soon rose to +0.5° where it remained for some time, and then gradually rose toward the end of the distillation. If hydrogen telluride is allowed to diffuse into the tube *K* that surrounds the thermometer, tellurium will be deposited upon the thermometer and the inner wall of *K*, and will render it impossible to read the thermometer. This is prevented by passing a current of hydrogen in at *N*. These determinations were made with a toluene thermometer, and absolute accuracy is not claimed for them. The gradual changes of temperature during the melting and the boiling of the hydrogen telluride are possibly due to the fact that there was no means of stirring the liquid.

Ernyei[1] gives —54° as the melting point of hydrogen telluride and states that the boiling point of the compound lies above 0°. A melting point of —48° and a boiling point of 0° are given by de Forcrand and Fonzes-Diacon,[2] but they do not state how the measurements were made.

(*c*) *The Action of Light upon Hydrogen Telluride.*—De Forcrand and Fonzes-Diacon[3] state that the decomposition of hydrogen telluride is accelerated by the action of light. The same statement appears in an article by Hempel and Weber.[4] In the hope that the gas might prove stable at ordinary temperatures in the absence of light, and thus permit of the determination of its density in light-tight containers, an examination of the extent to which the decomposition of the gas is retarded by the exclusion of light was made.

A small amount of hydrogen telluride was prepared by the electrolytic method already described. The gas was dried and condensed in the usual manner, and was then distilled through a series of bulbs that were sealed to the outlet tube of the condensation tube. The row of bulbs was placed in an inclined position to facilitate the displacement of the hydrogen in the bulbs by the heavier hydrogen telluride. The bulbs, filled in this manner with pure, dry hydrogen telluride, were sealed off with a very small blast flame applied to the constrictions in the tubes that connected the bulbs. The preparation of the gas and the sealing of the samples were carried on in faint red light. Two of the bulbs were placed in diffused daylight, and two were kept in the dark. All of the four bulbs were examined in red light at the end of half an hour and again at the end of ten hours. It was observed that at the end of half an hour there had occurred in all four of the bulbs an amount of decomposition of hydrogen telluride sufficient to give a visible deposit of tellurium upon the walls of the bulbs. At the end of ten hours the walls of all the bulbs were covered almost completely with a mirror-like deposit of tellurium. So far as the eye could judge, the deposit of tellurium in the bulbs that had been kept in the dark was quite as heavy as in those that had been exposed to the light.

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[1] *Z. anorg. Chem.*, **25**, 313 (1900).

[2] *Annales chim. phys.*, [7] **26**, 258 (1902).

[3] *Loc cit.*

[4] *Z. anorg. Chem.*, **77**, 48 (1912).

Summary.

1. Magnesium telluride and aluminum telluride were prepared, and the production of hydrogen telluride from aluminum telluride was studied.

2. Hydrogen telluride that was prepared from aluminum telluride was fractionally distilled, and the atomic weight of the tellurium in the fractions was determined by use of the ratio Te : TeO_2.

3. A new form of apparatus for the electrolytic preparation of hydrogen telluride was devised, and about forty grams of the gas were prepared.

4. Hydrogen telluride prepared by electrolysis was fractionally distilled, the fractions were decomposed by passing the gas into nitric acid, and the atomic weight of the tellurium in the several fractions was determined by titration of tellurium dioxide with potassium permanganate.

5. Solidified hydrogen telluride is a white crystalline substance that melts to a liquid of a very pale yellow color. Tellurium dissolves in liquefied hydrogen telluride, and the color of the liquefied gas seems to be due to the presence of this dissolved tellurium.

6. Determination of the melting point of hydrogen telluride gave a result of $-57°$; the boiling point was found to be $0°$.

7. Hydrogen telluride in sealed tubes slowly dissociates. This decomposition of the gas is not materially retarded by the exclusion of light.

8. The results of the investigation indicate that the hypothetical element, dvi-tellurium, does not exist.

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SOME ERRORS IN THE DETERMINATION OF THE RARE EARTHS AS HYDROXIDES.

BY T. O. SMITH AND C JAMES

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The writers have observed that, when the rare earths are precipitated as the hydroxides and ignited to oxides, the results are higher than when they are precipitated as oxalates and ignited. Moreover, the former method gives results which are not concordant with varying amounts of the precipitant. Since this method has been often recommended for quantitative determinations it seemed desirable that a careful investigation should be carried out.

As a basis for determining the source of error it was thought advisable to compare the following precipitants: oxalic acid, ammonium oxalate, sodium hydroxide and ammonium hydroxide. If the cause of error were due to the formation of a basic salt, lanthanum being the most powerful base of the rare earths, would tend to give a maximum. It seemed preferable to use lanthanum chloride rather than lanthanum nitrate, since lanthanum hydroxide upon ignition would hold chlorine more readily than nitric acid.

A solution of pure lanthanum chloride was prepared by igniting a very pure lanthanum oxalate, dissolving the resulting oxide in a minimum amount of dilute hydrochloric acid, evaporating to dryness and taking up in water. The solution was made faintly acid, by a few drops of hydrochloric acid, to convert any traces of basic chloride back to the normal salt.

Oxalic Acid.—Varying amounts of the lanthanum chloride solution were measured out and precipitated in the cold by the addition of a slight excess of oxalic acid. The volumes in each case were kept constant so as to remove any doubt as to solubility. The precipitated solutions were allowed to stand over night. The oxalate was filtered off, washed with cold water, dried and ignited.

The results follow:

No	Cc $LaCl_3$	Wt. of oxide.	Oxide per cc
1	25	0.0866	0.003464
2	25	0.0864	0.003456
3	50	0.1729	0.003458
4	50	0.1732	0.003464
5	50	0.1729	0.003458
6	75	0.2594	0.003459
7	75	0.2596	0.003461
Average			0.003460

Ammonium Oxalate.—In order to avoid the formation of free hydrochloric acid and consequent possible solubility of the oxalate during precipitation, ammonium oxalate was employed as reagent. The operations were identical with the above, except for the substitution of ammonium oxalate for oxalic acid.

The results follow:

No.	Cc. $LaCl_3$.	Wt. of oxide.	Oxide per cc.
1	50	0.1725	0.003450
2	50	0.1726	0.003452
3	25	0.0864	0.003456
4	25	0.0865	0.003460
5	50	0.1729	0.003458
6	50	0.1730	0.003460
7	50	0.1728	0.003456
8	75	0.2594	0.003459
9	75	0.2592	0.003456
Average (omitting 1 and 2)			0.003458

Sodium Hydroxide.—Varying amounts of the lanthanum chloride solution were taken, diluted, precipitated at the boiling point, filtered, washed with hot water, dried and ignited.

The following figures were obtained:

No.	Cc LaCl$_3$	Wt of oxide.	Oxide per cc.
1	25	0.0878	0.003512
2	50	0.1751	0.003502
3	75	0.2619	0.003492
Average			0.003502

The variation of these results with each other suggested precipitation with different amounts of the reagent. Three 50 cc. portions were taken, diluted and precipitated at the boiling point with a measured slight excess of sodium hydroxide solution. Three other 50 cc. portions were taken, diluted, heated to boiling and precipitated with double the amount of sodium hydroxide.

The data follow:

No	Cc LaCl$_3$	Wt of oxide	Oxide per cc.
1	50	0.1751	0.003502
2	50	0.1753	0.003506
3	50	0.1755	0.003510
Average			0.003506
4	50	0.1772	0.003544
5	50	0.1771	0.003542
6	50	0.1768	0.003536
Average			0.003541

Ammonium Hydroxide.—Varying amounts of the lanthanum chloride solution were taken, heated to boiling, precipitated with a slight excess of ammonium hydroxide, filtered, washed with hot water, dried, and ignited.

The results follow:

No.	Cc LaCl$_3$	Wt of oxide.	Oxide per cc.
1	25	0.0870	0.003480
2	25	0.0871	0.003484
3	50	0.1740	0.003480
4	50	0.2612	0.003484
5	75	0.2612	0.003483
6	75	0.2616	0.003488
Average			0.003483

When the results of the various precipitants are compared the following facts are brought out: Ammonium oxalate gives figures similar to oxalic acid with the exception that when an excess of ammonium oxalate is used the precipitate carries with it some ammonium oxalate. Upon washing the precipitate with water the complex, ammonium lanthanum oxalate, appears to undergo hydrolysis. When this takes place some lanthanum oxalate is produced in such a fine state of division that it passes through the filter paper. The first two results among the ammonium oxalate determinations illustrate this fact. It was observed that these filtrates were somewhat opalescent.

The amounts of oxide are high when sodium hydroxide is used. This is evidently not due to the formation of a basic salt since when a large amount of sodium hydroxide is used still higher results are obtained. The above facts indicate the carrying down of sodium. In order to prove the presence of sodium in the oxide it was dissolved in hydrochloric acid and the solution tested for sodium by means of the flame coloration and the spectroscope. Both gave very decided tests for sodium.

Ammonium hydroxide was substituted for sodium hydroxide because of its volatile nature. But in this case also high results were obtained although not as high as when sodium hydroxide was used. A qualitative analysis of the lanthanum hydroxide revealed traces of chloride which would indicate the formation of a certain amount of basic chloride. It is highly probable that ammonium hydroxide would give quantitative results if the lanthanum were present as the nitrate because upon ignition the basic nitrate, if formed, would be readily broken down to oxide.

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THE PREPARATION AND PROPERTIES OF SODIUM ZINC CYANIDE.

By NATHANIEL HERZ.

Received March 16, 1914.

Previous Work.—In THIS JOURNAL,[1] W. J. Sharwood gave a summary of previous work, and the results of his own experiments on the preparation of sodium zinc cyanide. Both his results, and those of Rammelsberg, quoted by him, indicate the existence of a compound, $NaZnCy_3.2^1/_2H_2O$, which is very difficult to crystallize, while the mother liquor has the composition Na_2ZnCy_4, agreeing with the compound existing in dilute solutions, and also with the corresponding potassium compound. None of these preparations analyzed, however, gave satisfactory molecular ratios either for the salt, or for the water of crystallization, the crystals being highly efflorescent.

One of the greatest difficulties in this preparation was due to impurities in the sodium cyanide then available. The material then on the market contained appreciable quantities of potassium cyanide and of carbonates, causing the crystallization of the double potassium salt or of sodium carbonate. The compound crystallized in the most successful trials may have been influenced by the presence of free alkali in the solution. Recently it was suggested by Mr. Sharwood that it might be possible to prepare a purer solution with the high-grade commercial sodium cyanide now on the market, and thus find out whether the double cyanide splits up on crystallizing into $NaZnCy_3$ + NaCN, or whether at some point Na_4ZnCy_4 can be crystallized. The commercial sodium cyanide now sold as equivalent to "128 130% KCN" contains about 97% NaCN, with some carbonate and moisture, and only traces of potassium and sulfide.

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[1] Vol. 25, 570–596 (1903), "A Study of the Double Cyanides of Zinc with Potassium and with Sodium."

Preliminary Experiments.—The principal points to consider in this preparation are as follows: The starting point is zinc cyanide, $ZnCy_2$, which should be free from potassium (left in it by the precipitant used) and from carbonate; it should be as free from basic cyanide as possible. It hydrolyzes very easily on washing. The zinc cyanide is dissolved in sodium cyanide solution, which must also be free from potassium and carbonates. By using an excess of zinc cyanide, the solution can be saturated with zinc, without attacking much of the hydroxide of the basic cyanide, which would otherwise dissolve with the formation of sodium zincate. The excess of zinc cyanide also reacts with any free alkali present, forming double cyanide and zinc hydroxide.

The first attempt was made with quantities such as to give about 25 grams of anhydrous Na_2ZnCy_4. The zinc cyanide was first prepared by dissolving zinc chloride in boiled water, acidified with a little hydrochloric acid. The free acid insured the presence of hydrocyanic acid in the solution after precipitation, lessening the tendency toward hydrolysis on washing. The precipitant was a solution of sodium cyanide, which had been treated with a slight excess of lime and filtered to remove carbonates. The solution was stirred vigorously while precipitating, and filtered with the aid of suction. The precipitate was then washed, starting with warm and finishing with cold, recently boiled distilled water. The zinc cyanide was then digested with a solution of sodium cyanide, also treated with lime to remove carbonates. Then the solution was filtered, evaporated to a sirupy condition, and placed in a vacuum desiccator over concentrated sulfuric acid. After a few days a white layer was seen on the surface of the solution, which may possibly have been the compound $NaZnCy_3$ as described by previous investigators. It was not further examined, however, as upon attempting to remove this film for investigation, it was found that below the surface there was a good crop of diamond-shaped crystals that were invisible when in the solution on account of having the same index of refraction as the strong solution. These crystals were removed, drained, dried on filter paper, and analyzed, with the following results:

	H_2O.	CN.	Zn.	Na (by diff).
Per cent	20.20	39.44	24.60	15.76
Molecular ratio	2.95	4.03	1.00	1.82

These results indicate a compound, $Na_2ZnCy_4.3H_2O$, agreeing in composition with the solution. As the material was not sufficient for further investigation, a second preparation was made.

At this point an experiment was tried to determine whether any interference might be expected from the small amount of calcium left in the solution from the treatment with lime for removing carbonates. It was found that the double cyanide formed by digesting lime with a large excess of zinc cyanide was so soluble as to be almost impossible to crystallize, so this possible interference need not be considered.

Final Preparation.—The method used was similar to that outlined above, but the quantities used were three times as great. Two crops of crystals were obtained, but they were not recrystallized, as the quantity was too small for a salt of such high solubility, and the solution was sufficiently pure to insure very little contamination. Water of crystallization was determined by drying to constant weight at 105°. Cyanogen was determined by titration with $N/20$ silver nitrate solution, using potassium iodide as indicator, in the presence of sufficient ammonia to counteract the effect of the zinc. The solution was standardized under similar conditions by a solution of cyanide of known strength, to which an equivalent amount of zinc was added. Zinc was determined by titration with standard potassium ferrocyanide in acid solution, using uranium nitrate as an outside indicator. Sodium was determined in the last analysis by weighing the sulfates of sodium and zinc together, and subtracting the zinc sulfate as determined by the zinc titration. In other cases, sodium was taken by difference. All titrations were made on aliquot parts of the same solution, and water of crystallization was determined on a different sample, as it was not considered safe to dissolve the residue from the water determination and use it for analysis, although no appreciable decomposition was noted. The greatest difficulty was experienced because of the rapid efflorescence of the crystals, making it almost impossible to weigh out two portions with the same water content.

TABLE OF ANALYSES.

The figures in parentheses indicate the number of closely agreeing determinations averaged.

	Per cent.				Molecular ratios.			
	H_2O.	Zn.	CN.	Na.	Na.	Zn.	CN.	H_2O.
	(3)	(2)	(2)					
First crop of crystals	19.95	23.81	37.24	19.00	2.20	1.00	3.85	2.96
First crop. Selected material.	(1)	(2)	(3)					
Partly effloresced	19.80	24.05	38.15	18.00	2.06	1.00	3.88	2.91
	(1)	(2)	(3)	(1)				
Second crop (Total = 99.5%)	20.02	23.93	38.67	16.88	1.98	1.00	4.02	3.07

Solubility.—The specific gravity of a saturated solution at 15° was found to be 1.37. A portion of this solution was weighed and zinc determined. Calculated to Na_2ZnCy_4, the results are as follows: One part of the anhydrous salt is soluble in 0.83 part of water at 15°, and one part of the hydrated salt, $Na_2ZnCy_4.3H_2O$, is soluble in 0.47 part of water.

Crystalline Form.—A few of the best crystals were selected for measurement. The measurements were kindly made by Prof. W. E. Ford and Dr. W. M. Bradley, of the Sheffield Scientific School, Yale University. As the crystals effloresced to some extent in transit, some of the angles could not be measured with as great precision as desirable.

The system of crystallization is orthorhombic. The angles are:

Base (001) to pyramid (111)........	$c \wedge p$	62° 50.5′
Pyramid (111) to pyramid (111)	$p \wedge p$	103° 49′
Pyramid (111) to brachypinacoid (011).. .	$p \wedge b$	64° 16.5′

One other form, the brachydome (010) also occurs.

The axial ratio is $a : b : c = 0.56 : 1.00 : 0.95$

The simplest crystal consists of a prominent unit pyramid (111) and base (001) (Fig. 1). In the larger crystals modifications appear, consisting of the brachypinacoid (011) and the brachydome (010) shown in Fig. 2.

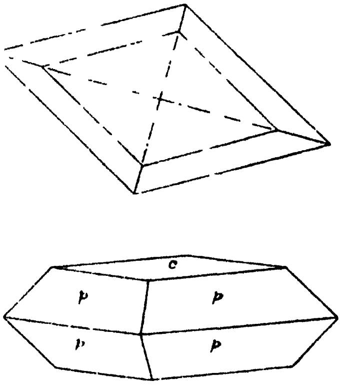

Fig. 1.

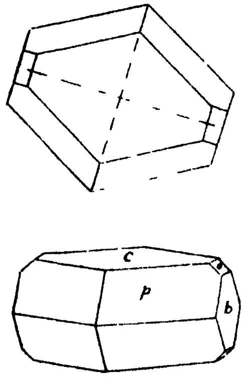

Fig. 2.

The pseudo-hexagonal plan is characteristic of the larger crystals, as is the diamond shape of the smaller ones. The largest crystals obtained were about 5 mm. long.

Conclusions.—From pure solutions of sodium zinc cyanide, free from less soluble salts and from excessive amounts of free alkali, the compound that crystallizes is $Na_2ZnCy_4.3H_2O$.

The hydrated salt is soluble in less than half its own weight of water. The crystals are orthorhombic, simple in form, either flat diamonds or pseudo-hexagonal plates. They are brilliant when removed from the solution, but effloresce rapidly, becoming dull and chalky. The dry salt is quite stable in air, being completely soluble in water after several days' exposure. Even after complete dehydration at 105°, there was very little evidence of decomposition. When working with pure solutions, no evidence was found to indicate the separation of the compound $NaZnCy_3.2^1/_2H_2O$ as obtained by previous investigators.

LEAD, SOUTH DAKOTA.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS (PUBLICATION NO. 17) AND FROM THE NATIONAL BUREAU OF STANDARDS.[1]]

COMPARISON OF THE SILVER AND THE IODINE COULOMETERS[2] AND THE DETERMINATION OF THE VALUE OF THE FARADAY.

BY STUART J. BATES AND GEORGE W. VINAL

Received March 16, 1914

Introduction.

Of the many electrochemical reactions which may theoretically be employed to determine the Faraday, *i. e.*, the quantity of electricity associated with a chemical equivalent in any electrochemical change, that of the deposition of silver from a solution of silver nitrate is the only one that has been extensively investigated. The values which have been accepted for the Faraday from time to time, have almost entirely been based upon results with the silver coulometer. This naturally resulted from the fact that the international ampere is defined in terms of the silver deposited under more or less rigorously fixed conditions and, hence, this instrument has been the subject of many thorough investigations, both by the National Standardizing Laboratories and by private individuals. As a result of these investigations it has been possible, for the past few years so to define the conditions to be used in connection with the silver coulometer that a reproducibility of 1 or 2 parts in 100,000 may be obtained. Until recently no other coulometer had attained anything approaching such a degree of precision.

A little over a year ago, however, Washburn and Bates[3] published the results of a study of an iodine coulometer which they had devised and which was found to have a reproducibility of the same order as that of the silver coulometer. The apparently complete reversibility and purity of the electrochemical reaction in the iodine coulometer, coupled with the fact that no solid deposit is obtained, made it a particularly valuable reaction to employ for determining the Faraday, and warranted very exact electrical measurements. Since the Bureau of Standards had, as a result of recent work on the silver coulometer, exceptional facilities for such measurements, arrangements were made for the comparison of the silver and the iodine coulometers at the Bureau of Standards during the summer of 1913.

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Although the word voltameter is still in quite extensive use, and on account of the decision of the London Conference is employed in the Bulletins of the Bureau of Standards, the name coulometer is employed throughout this paper. This word appears more appropriate because it is coulombs which the instrument directly measures, and because of the possibility of confusion between the words voltameter and voltmeter.

[3] THIS JOURNAL, 34, 1341, 1515 (1912).

I. Description of the Electrical Circuit.

The methods of determining the strength of the currents and the arrangement of the circuit were in principle the same as those previously employed at the Bureau of Standards in the investigation on the silver coulometer.[1] Certain modifications were necessary, however, owing to the high resistance of the iodine coulometers and the smaller currents to be employed. An electromotive force of 240 volts was used to pass a current of one-fourth of an ampere through the circuit containing the coulometers and the ballast resistance of about 400 ohms. This necessitated particularly high insulation, owing to the damp weather which is prevalent in Washington in summer. Fortunately this was obtainable by mounting the galvanometers and all apparatus on paraffin and using paraffin insulators to support all wires pertaining to the circuit. The circuit is shown diagrammatically in Fig. 1. The current was measured by means of a Wolff potentiometer (P), and also by directly balancing the electromotive force of a Weston standard cell (No. 109), maintained at 28° in oil, against the fall in potential across two 2-ohm resistance standards (R) through a second galvanometer, similarly to the method previously described.[2] To eliminate the errors of the potentiometer, however, the dials were set to the voltage of the cell as nearly as possible and balanced with the standard cell on the same terminals to which the

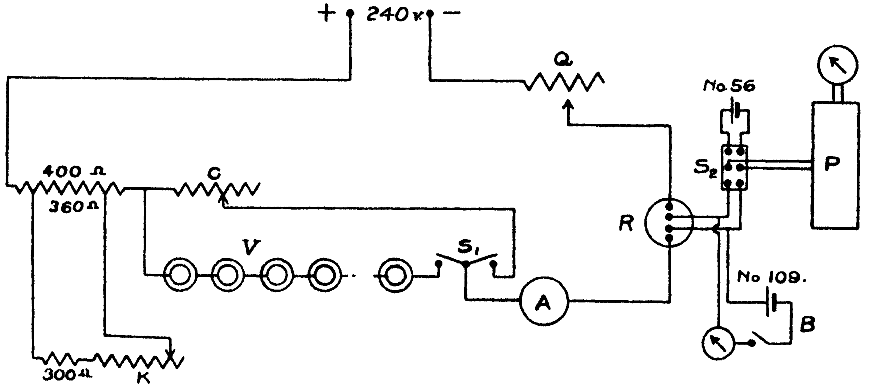

Fig. 1.

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[1] Rosa and Vinal, *Bull. Bur. Standards*, 9, 152 (1912).

[2] *Ibid.*, 9, 179.

electromotive force of the standard resistance was applied. To facilitate this, a double pole, double throw switch (S_2), with all joints soldered and embedded in paraffin, was used. (Q) is a series resistance for quick adjustment of the current, (A) is an ammeter, (C) the compensating resistance, usually about 590 ohms, and (K) is a Kelvin rheostat for fine regulation. In the case of those runs in which the standard cell and resistance were used to measure the current, the time was accurately determined by means of the arrangement previously employed.[1] The quick, double pole, double throw switch (S_1), which serves to throw on or off the circuit through the coulometers, simultaneously closes another circuit which operates one of the pens of the chronograph.

As a test of the circuit, a comparison of the two methods of measuring the current was made when the humidity was 75%; they agreed to within two parts in a million. All of the experiments were made under lower humidity conditions; when necessary, refrigerating coils were used to reduce the humidity of the room.

As the potassium iodide solution in the iodine coulometers has a high temperature coefficient of conductivity, and was subject to considerable heating by reason of its high resistance, some trouble was anticipated in maintaining the current at constant value, but this was avoided by immersing the iodine coulometers to a little above the V-tube in large water baths. At the beginning of an experiment the drift in current, due to heating in the coulometers, was rapid for about five minutes. After this time it decreased and finally became surprisingly steady during the greater part of the experiment.

Some of the experiments were at $^1/_4$ ampere for four hours. In all of these, except the first two, the current was maintained constant during the experiment. In the other experiments a current of $^1/_{20}$ ampere was used for 20 hours but the current was not measured against the standard cell and resistance. For the purpose of computing the value of the Faraday it is not necessary to measure the current by means of the cell and resistance. It was, however, deemed advisable to do so in some cases at least so that the silver coulometer determinations might be compared with previous work at the Bureau of Standards. For this purpose the same standard cell and resistances as were employed in the previous investigation were used. Comparisons of these with the standards maintained at the Bureau showed only very slight changes to have taken place.

II. The Coulometers.

A. *The Iodine Coulometers.*

1. Apparatus and Manipulation.—The three iodine coulometers used were of the same type as those previously employed by Washburn and Bates. The apparatus, which is shown in Fig. 2, consists essentially of

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[1] *Bull. Bur. Standards*, 9, 177.

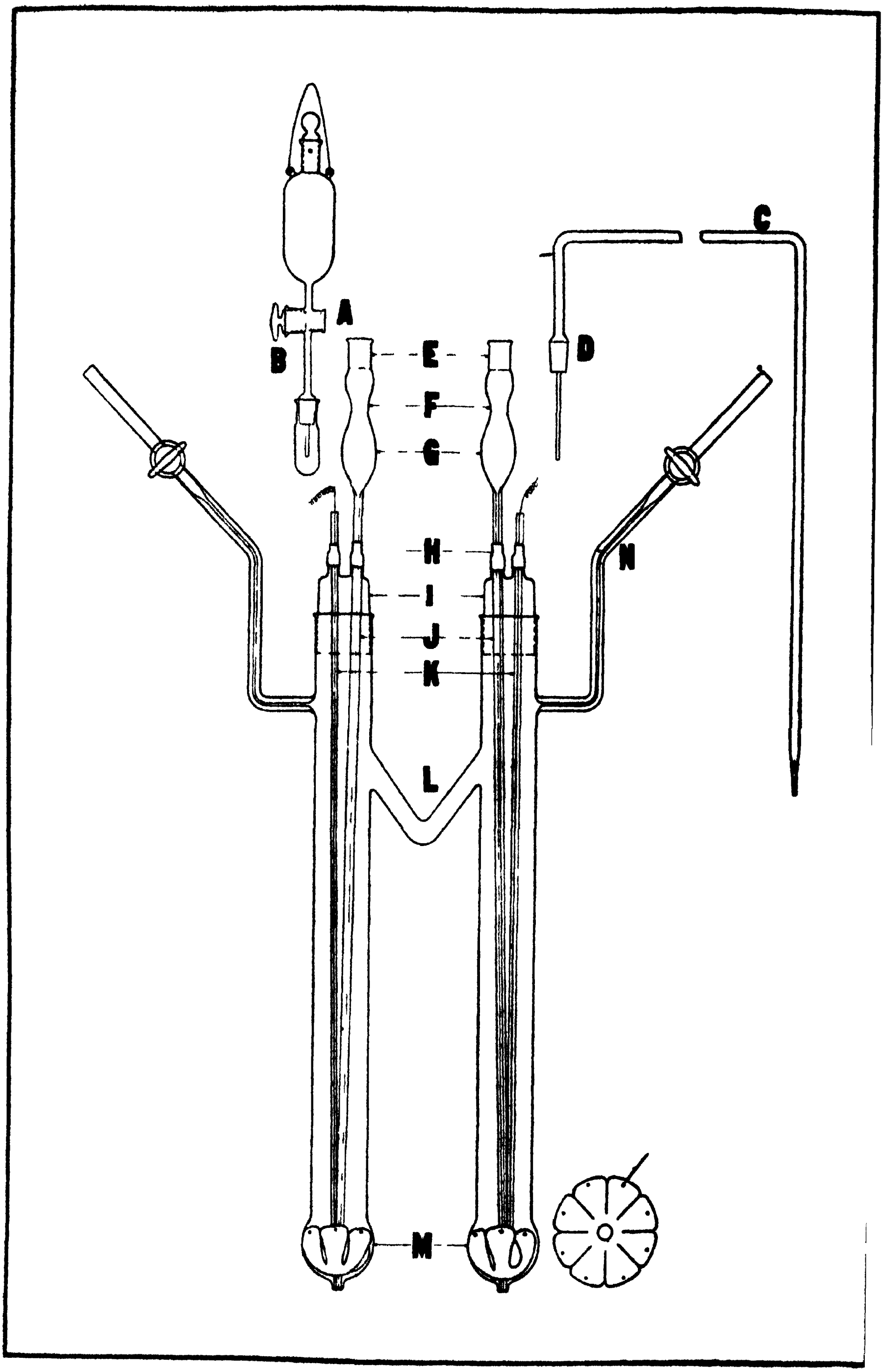

Fig. 2.

two upright limbs connected by a V-tube. At the bottom of each limb is an electrode (*M*). The anode consists of a platinum iridium alloy, it having been found that iodine is without appreciable effect on such an electrode, though one of pure platinum is attacked. Since the cathode solutions were not to be analyzed in the present investigation, it was permissible to use platinum electrodes for the cathode. The electrodes were sealed into glass tubes (*K*) through which ran the electrical connections to the outside. These tubes, as well as the capillary tubes (*J*) through which the solutions were poured around the electrode, come out through small openings in the caps (*I*) at the top of the limbs. The joints between these tubes and the caps are made air-tight by means of short pieces of rubber tubing.

In order to prevent diffusion within the coulometer, and also to prevent rapid changes in the resistance of the coulometers due to heating, they were placed in large battery jars filled with water. The coulometers are filled and the solutions removed for analysis in a manner similar to that employed in the previous investigation.[1] A 10% solution of potassium iodide is poured through the side tube (*N*) into the coulometer until it is filled to a little above the V-tube (*L*). There is then poured under this solution and around the anode (*M*) 25 cc. of a concentrated solution of potassium iodide (1 g. of salt to 1 g. of water), which is admitted through the bulb (*G*) and the capillary tube (*J*). In a similar manner, about 10 cc. of this concentrated solution, followed by 20 cc. of a concentrated solution of iodine in potassium iodide solution, are placed around the cathode. During a run the iodine in both limbs remains well at the bottom. After the first weighing of one of the silver coulometers at the conclusion of a run the approximate amount of iodine formed, and then the approximate amount of arsenious acid solution required for the titration, was calculated. About one drop less than this amount is weighed out into a liter Erlenmeyer flask, and disodium phosphate solution added to control the hydrogen ion concentration. The flask is then fitted to the delivery tube (*C*) so that the tip of the tube is below the level of the liquid and the anode solution quietly pulled up the capillary tube and over into the flask by applying a gentle suction to the latter. The solution is then mixed and the titration completed in the manner described below.[2]

2. *Chemicals and Solutions.*—The water employed for all of the solutions used in connection with the work of the iodine coulometer was obtained by redistilling the distilled water of the laboratory from alkaline permanganate, the first and last fractions of the distillate being discarded.

The potassium iodide was obtained by recrystallizing J. T. Baker's product until it was no longer alkaline to phenolphthalein. Because of the damp weather prevalent during this investigation, the potassium iodide was kept in desiccators over calcium chloride.

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[1] THIS JOURNAL, 34, 1359 (1912).

[2] Page 924.

The concentrated iodine solution which was used for surrounding the cathode electrode was prepared by dissolving 910 g. of iodine and 585 g. of C. P. potassium iodide in 320 g. of water. The dilute standard iodine solution was prepared by diluting the concentrated solution till it was about 0.01 normal. Its strength was determined by titrating it against the dilute standard arsenious acid solution.

The standard arsenious acid solution was prepared by dissolving 240 g. of Kahlbaum's arsenious acid, which had been recrystallized from conductivity water in a solution containing 120 g. of J. T. Baker's C. P. sodium carbonate. The solution was then made up to approximately five liters and kept in a five-liter glass bottle. The bottle was fitted with a delivery tube containing a stopcock and with a three-way tube through which hydrogen passed as the solution was withdrawn by means of the delivery tube. This three-way tube was attached to a manometer to indicate the pressure of hydrogen within the bottle and to Geissler bulbs which contained some of the same solution that was in the bottle and through which the hydrogen bubbled before entering the bottle.

It had been discovered in the previous investigation that the arsenious acid solution slowly oxidized. Hence, before beginning this investigation, the solution was practically freed from dissolved air by slowly bubbling hydrogen through it. This was led in by means of the tube which afterwards served as the delivery tube, and which reached to the bottom of the bottle. After hydrogen had been bubbling through the solution for 24 hours, the stream of hydrogen was attached to the Geissler bulbs, care being taken that no air was permitted to enter the bottle. The pressure of hydrogen within the bottle was then raised to and maintained at a pressure of 4 to 5 cm. of mercury above atmospheric pressure.

The hydrogen which was used for this purpose was prepared from C. P. zinc and sulfuric acid in a Kipp generator. It was passed through a wash bottle containing alkaline permanganate and then over reduced copper contained in a quartz tube. This tube and the copper were kept red hot throughout the course of this investigation by means of an electric heating device. From the quartz tube the hydrogen was led to the bottle containing the standard solution by means of flexible copper tubing.

The bottle was kept in a large vessel of about 20 liters capacity. This vessel was filled with water to prevent condensation of moisture on the upper part of the inside of the bottle as a result of temperature changes in the surroundings. The whole was mounted on a turn-table in such a manner that the delivery tube might be swung directly over the mouth of a flask resting on the pan of a large Ruprecht balance.

The dilute arsenious acid solution was prepared by diluting about 10 g.

of the standard solution to 100 times its weight. This solution was not protected from the air and since it slowly oxidized, a fresh lot was prepared every week or ten days. It was compared with the dilute iodine solution every 3 or 4 days. In this way it was possible to determine the strength of the solutions, so that no error greater than 5 parts in a million was introduced because of a change in their concentration.

3. Methods of Standardization and Analysis.—For the careful standardization of the arsenious acid solution, it was necessary to prepare a quantity of pure iodine. For this purpose, potassium permanganate was added to a dilute sulfuric acid solution containing an excess of potassium iodide and the precipitated iodine, after having been washed by decantation till the wash-water was practically neutral, was dried in the centrifuge. It was then distilled from a retort and caught in a molten condition in a flask. The iodine was broken up in a dry mortar and kept in a desiccator over sulfuric acid, being sublimed as needed. The sublimation apparatus (Fig. 3) consisted of a tube of Jena geräteglas about 100 cm. long and 3 cm. diameter. Into one end of it fitted a ground glass stopper through which a current of air could be passed. This air was bubbled through a solution of alkaline permanganate, through two wash bottles containing sulfuric acid and then passed through a tube containing phosphorus pentoxide which had been recently sublimed into it. At the end nearest to the subliming apparatus this tube was closed by means of a stopcock, which was joined with Khotinski cement to the glass stopper of the subliming tube. During the course of the experiments very little moisture reached the phosphorus pentoxide and that only at the end farthest from the subliming apparatus.

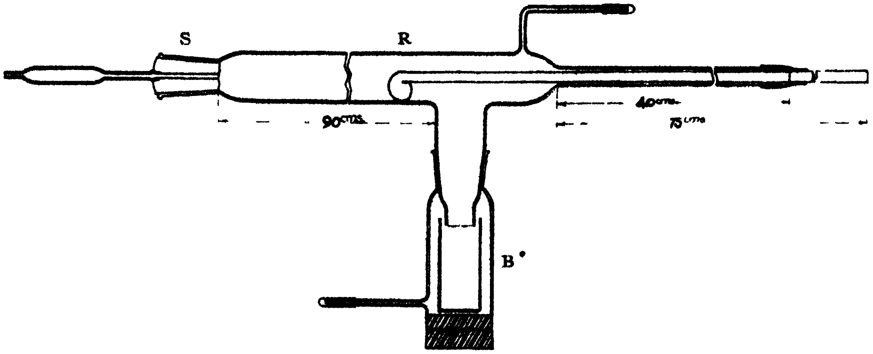

Fig. 3.

The iodine in a porcelain boat is placed inside the sublimation apparatus just ahead of the glass stopper (*S*). Movable heating coils of manganin wire serve to sublime the iodine from this position down the length of the tube. The rate of sublimation could be conveniently controlled by regulating the temperature of the heating coils and the current of air passing through the tube. In passing from one end to the other of the sublimation apparatus the iodine was sublimed at least three times. It was then transferred, without exposure to the atmosphere of the room, into a previously weighed quartz weighing bottle, (*B*), by means of a rake, (*R*), which was operated through a narrow tube some 40 cm. in length sealed onto the subliming tube.

The iodine was weighed in the constant temperature room on the Oertling balance which has been previously described.[1] When empty the weighing bottles were always left on the balance pan at least four hours before a weighing was attempted; when they contained iodine they were left over night. The weighings were made by substitution, an empty weighing bottle serving as part of the counterpoise. The set of weights employed had been compared with the standard weights of the Bureau. It is believed that the weight of iodine was known to 0.02 0.03 milligram.

For the first week or two of the present investigation, the iodine coulometers did not check well and the arsenious acid solution could not be accurately standardized. It was found that the trouble lay in the method of weighing the solution. Up to June 26th the method was that employed in the previous investigation at the University of Illinois. Liter Erlenmeyer flasks were balanced on the two pans of a large Ruprecht balance, the desired amount of solution run into the flask on the left-hand pan, a rubber stopper which had been weighed with the flask inserted into its mouth and the weight of the added solution determined. The previous work had been done during the spring of the year in a basement room which was not heated artificially. The room was quite cool and the variation in the amount of evaporation of the solution during the time required to draw off the solution and stopper the flask was not sufficient to introduce an error greater than 0.002%. The temperature of the room in which the weighings for the present investigation were made was between 29° and 31°. This caused an uncertainty in the weighing which depended upon the length of time it took to transfer the proper amount of solution to the flask and to stopper it. This time was somewhat variable, since toward the end of the addition of the solution to the flask it had to be added slowly, in order to get the weight within 0.1 g. of that required for the titration, before the final weighing to a few tenths of a milligram was attempted.

This uncertainty in the weight of the standard solution was greatly reduced by the following modification in the method of weighing. About 25 cc. of water were added to both of the flasks on the balance pan, they were then balanced and it was determined whether or not the rate of evaporation of water from both of them was the same. The mouth of the counterpoise flask was somewhat larger than that of the flasks in which the solution was weighed, so it lost weight more rapidly. However, by adjusting the size of the opening by means of a small piece of paper the rate of evaporation from the two flasks could be practically equalized.

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[1] *Bull. Bur. Standards,* 9, 174 (1912).

The required amount of solution was then added, both flasks left unstoppered and the weight determined as soon as possible. The rate of evaporation was again investigated, and if it were not the same as it was before the solution was added, an allowance was made for this. The uncertainty in the weight of solution taken was seldom over 0.5 milligram but is probably the greatest source of error connected with the iodine coulometers in this investigation. With practice this error was reduced since towards the end of this investigation both the coulometers and the standardizations checked to 1 or 2 parts in 100,000.

After the arsenious acid solution was weighed out, the required amount of disodium phosphate solution was added to the flask. In the case of the standardizations some 30 g. of potassium iodide were also added, and then the quartz weighing bottle was introduced into the flask and opened below the level of the liquid to prevent any loss of iodine vapor. When the iodine had completely dissolved, water was added till the volume of the solution was 250 to 275 cc. The dilute arsenious acid solution was then run from a buret into the flask, till the iodine color all but disappeared and the solution was set aside for 3 to 5 minutes for equilibrium conditions to be attained. For the completion of the titration the flask containing the solution and another containing the same volume of water were set side by side on a large sheet of unglazed white paper before a north window. The arsenious acid solution was then added drop by drop till the color of iodine just disappeared. It was possible by proceeding in this way and by comparing the appearances of the liquids in the two flasks to detect the effect of a single drop of the arsenious acid solution upon the iodine color. After determining the end point about 1 cc. of the dilute iodine solution was run in and the end point again determined. In this way three or more observations were always obtained for each end point; with practice and with favorable illumination it was possible to decrease the uncertainty in the end point to 0.02–0.03 cc. of the dilute arsenious acid solution. This corresponds to an uncertainty in the titration of 5 or 6 parts per million.

4. *Strength of the Standard Arsenious Acid Solution*—The data obtained for the standardization of the arsenious acid solution are given in Table I. This table is divided into two parts, corresponding to the two methods of weighing the solution. The first column gives the date of the standardization, the second the number of g. of iodine (corrected to vacuo by adding 0.0099% of the apparent weight) taken. In the third is found the number of g. of arsenious acid solution used in the titration; the fourth gives the g. of iodine corresponding to one g. of the standard solution;

this value will hereafter be referred to as the factor. The value for the factor, as calculated in the manner described below, is given in the next column and in the sixth is found the difference in percentage between the value of the factor as found and as calculated.

TABLE I.

	Iodine.	Arsenious acid solution.	Factor. Found.	Factor. Calc.	Difference in percentage.
		(*a*) First Period.			
June 4th	4.81605	44.5100	0.108201	0.108193	+ 0.008
June 7th	5.11905	47.3058	212	190	+ 0.020
June 11th	4.97658	46.0003	186	186	0.000
June 14th	2.89043	26.7085	221	183	+(0.035)
June 16th	5.96126	55.1136	163	180	— 0 016
June 19th	4.13730	38.2395	220	178	+(0.039)
June 21st	4.78222	44.2131	163	176	— 0.012
Average deviation					0 011
		(*b*) Second Period.			
June 30th	5.80150	53.6502	0.1081356	0.1081352	+ 0 0004
July 1st	5.73071	52.9967	334	343	— 0.0008
July 3rd	5.39535	49.8957	326	323	+ 0.0003
July 9th	4.50081	41 6258	254	266	— 0 0011
July 10th	5.41817	50.1110	233	256	— 0 0021
July 12th	4.64987	43 0048	244	237	+ 0 0006
July 16th	5.37630	49.7256	197	199	— 0.0002
July 17th	5.98294	55.3427	071	189	—(0.0109)
July 19th	5.78941	53.5518	086	170	—(0.0077)
July 21st	4.93161	45.6139	163	151	+ 0.0011
July 22nd	5.00639	46.3064	144	141	+ 0.0003
July 23rd	5.31224	49.1342	169	132	+ 0.0033
July 25th	5.15089	47.6395	222	112	+(0 0101)
July 28th	4.91674	45.4787	108	083	+ 0 0023
July 29th	4.70907	43.5590	078	074	+ 0 0004
July 30th	5.77480	53.4188	042	064	— 0.0020
July 31st	4.31213	39.8883	051	054	— 0 0003
Aug. 1st	5.18195	47.9361	012	045	— 0 0030
Aug. 2nd	5.55903	51.4236	027	036	— 0 0008
Average deviation					0.0012

The results show that even with the precautions taken the standard solution was oxidizing. In order to compare the standardizations and to determine the strength of the solution at any time, the values of the factor found in Column 4 were plotted against the corresponding days upon which the titrations were performed. It was found that for the period during which the second and more accurate method of weighing was employed, a straight line could be drawn through the points in a satisfactory manner. From this line the strength of the solution for any particular day may be read off or the factor may be calculated from the equation of the line. The value for the factor F on the tth day after June 30th is given by $F = 0.1081352 - 0.00000096t$, and, therefore, changes at a rate less than 0.001% a day. The values for the factor given in the fifth column of Table I were calculated by means of this equation.

Of the standardizations obtained by the second method of weighing, those of July 17th, 19th and 25th were not considered in placing the line, because they deviated widely from the other observations. That of July 17th is farthest from the calculated value, the difference being 0.011%. The average deviation of 0.0012% is about what would be expected from the uncertainties in weighing the iodine, in weighing the solution and in determining the end point.

For the first period, during which the method of weighing was unsatisfactory, it is extremely difficult to draw a line, in a manner similar to that drawn for the second period. The slope of such a line, however, should be the same as that for the second period, since the change in the method of weighing could not have influenced the rate of oxidation of the solution. Having thus obtained the slope of the line, its position was chosen so that the positive and negative derivations were equal. The value for the factor for this first period was determined graphically.

B. *The Silver Coulometer.*

1. *Forms Used.*—Two forms of silver coulometer were used in all experiments—Smith's new form and the porous cup form. Both of these have been described in detail elsewhere.[1] In the tables that follow in the next section, it will be seen that the results of the absolute runs made with these coulometers are in good agreement with the best previous work. As in the case of the third series of experiments published by Rosa, Vinal, and McDaniel, where the mean value of the Weston normal cell is given in terms of both forms of coulometers, so here, we have included in the mean both forms of coulometers in order to obtain the value of the silver with which to compare the mean iodine deposits.

2. *Materials, etc.*—The details of the manipulation of the coulometers and the preparation of materials have all been described before. The electrolyte was prepared from double distilled water and silver nitrate especially prepared and tested for acidity by iodeosine and for reducing agents by potassium permanganate as described by Rosa, Vinal and McDaniel.[2] The anode and cathode acidities of each voltameter were measured at the conclusion of the experiment. The mean acidity of the electrolyte at the beginning of the experiment and of the cathode acidity at the end of the experiment were thus determined for each voltameter, and corrections to the deposit could be made for the acid present according

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[1] *Bull. Bur. Standards*, **9**, 172 (1912), **10**, 480 (1914).

[2] *Ibid*, **9**, 524 (1912).

to the equation $Y = 4.5X$, where Y is the amount to be added to the deposit in parts per million and X the acidity of the electrolyte in parts per million. This correction was determined by Rosa, Vinal and McDaniel and is described by them.[1] In the present case the electrolyte was always very nearly neutral, so that the corrections are very small in all cases.

III. Tables of Results.

The details of each experiment made or attempted are given in Table II; a summary of the results is found in Table III. The experiment of June 6th which is designated as No. 1 we have omitted from Table III since, during the run, iodine from the cathode was seen to have migrated up this limb and over into the anode side, coloring the liquid in the connecting V-tube quite distinctly.[2] Before starting the experiment it had been suggested that the first run would be largely of a preliminary nature. Aside from this run the only silver coulometer measurements omitted in computing the results are those enclosed in brackets. One of them on July 22nd deviates from the mean by about four times the average deviation of the others and hence may be called a gross error. Two others on July 30th were found to be alkaline at the close of the experiment, which is sufficient reason for discarding them as was shown in previous investigations.[3] Owing to a miscalculation which resulted in much too little arsenious acid solution being weighed out for two of the coulometers of run No. 9, but one accurate analysis of the iodine formed in this experiment was obtained.

In the column of remarks the experiments designated as "absolute" are those in which the current was maintained constant during the entire time of the run and measured in terms of a standard cell and resistance. In the "comparative" experiments this was not done.

In Table III are contained the summarized results and the computed values for the ratio of silver to iodine, the electrochemical equivalent of iodine and the value of the Faraday. Column 1 gives the number of the experiment corresponding to the numbers given in Table II. Columns 2 and 3 contain the mean deposits of silver and iodine for each experiment. Under "calculated coulombs" we give the number of coulombs as calculated from the silver coulometer deposits, using the value 1.11800 mg. per coulomb as defined by the London conference. These are, therefore, in international units. We also give the coulombs as calculated from the measurement of current and time when the absolute runs were

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[1] *Bull. Bur. Standards,* 10, 482 (1914).

[2] This movement was prevented in subsequent runs by the addition of the few cubic centimeters of concentrated potassium iodine solution which was run into this limb just before the iodine solution. With this procedure, it was never possible to detect any coloration due to iodine more than one-third way up the cathode limb.

[3] Report of Int. Tech. Com., p. 157 (1912).

TABLE II.—GENERAL TABLE OF RESULTS.

		Silver voltameters.	Acidity.					Iodine voltameters.					
Date of run. 1913	No. of run	Form.[1]	Mean. Pts. in 10^8.	Correction. Mg.	Deposit corrected for acidity Mg.	Mean value. Mg	Average deviation. Pts. in 10^8	Date of titration. 1913	Factor.	Deposit. Mg.	Mean value. Mg.	Average deviation. Pts. in 10^8.	Remarks.
June 6	1	LNF	0.8	0.01	4079.20	4079 19	3_6	June 7	0 108190	4799.35	4799.58	4_0	Trial experiment, $^1/_4$ amp., 4 hours. Discarded experiment because mixing occurred in the iodine voltameters. Current not maintained constant
		LNF	0.8	0.01	4079.51					4799 82			
		LPP	0.7	0.01	4079.16								
		SPP	0 9	0.01	[4078.68]								
		SPP	0.9	0.01	4078 90								
13	2	LNF	0.4	0.01	4105.98	4105.82	5_4	14	0 108183	4828 76	4829 59	11_8	Comparative experiment, $^1/_4$ amp, 4 hours.
		LNF	0.6	0.01	4106.10					4830.24			
		SPP	1.2	0.02	4105.52					4829 77			
		SPP	1.7	0 03	4105.69								
18	3	LNF	0.2	0 00	4104.70	4104.69	1_8	20	0 108177	4828 38	4828 62	5_0	Absolute experiment, current steady $^1/_4$ amp, 4 hours.
		LPP	0.7	0.01	4104.79					4828 86			
		SPP	0.3	0.00	4104.65								
		SPP	0.1	0.00	4104.61								
26	4	LNF	0.6	0.01	4099.10	4099 03	2_7	28	0 1081371	4822 22	4822 24	2_6	Absolute experiment, current steady $^1/_4$ amp, 4 hours.
		LPP	1.2	0.02	4099.17					4822.42			
		SPP	0.9	0.01	4098.89					4822.08			
		SPP	1 8	0.03	4098.93								
July 1	5	LNF	1.1	0.02	4397.16	4397 11	1_4	July 3	0 1081323	5172 58	5172 73	2_8	Comparative experiment, $^1/_{20}$ amp., 20 hours.
		LPP	1.0	0.02	4396.99					5172.87			
		SPP	1.3	0.02	4397.15					[5169 85]			
		SPP	2.2	0.04	4397.16								

9	6	LNF	0.9	0.01	4105.32	4105.23	2_8	11	0.1081247	4828 54	4828 51	2_0	Absolute experiment, current steady 1/4 amp, 4 hours
		LPP	1.1	0.02	4105.33					4828.69			
		SPP	1 3	0.02	4105.20					4828 30			
		SPP	1.7	0.03	4105.08								
14	7	LNF	2 0	0.04	4122.86	4123 10	2_9	16	0.1081199	4849 35	4849 42	3_4	Comparative experiment, 1/20 amp., 20 hours
		LPP	2.5	0.04	4123.29					4849.67			
		SPP	3.5	0.06	4123.15					4849 24			
		SPP	5.0	0 09	4123 08								
18	8	LNF	1.9	0 03	4104.78	4104 75	4_8	19	0 1081170	4828.63	4828 60	0_8	Absolute experiment, current steady 1/4 amp, 4 hours.
		LPP	2 0	0.04	4105.09					4828.53			
		SPP	3.7	0 06	4104.60					4828 63			
		SPP	4 0	0.07	4104 54								
22	9	LNF	..		4184.27	4184 24	2_6	24	0 1081122	[4920 91]	4921 30		Comparative experiment, 1/20 amp, 20 hours. Omit LPP determination
		LPP	3 5	0.06	[4184 94]					[4920 99]			
		SPP	1 2	0 02	4184 35					4921 30			
		SPP	1 2	0.02	4184 10								
25	10	LNF	0 1	0 00	4100 27	4100 27	2_4	26	0 1081102	4822 36	4822 47	1_4	Absolute experiment, current somewhat unsteady, 1/4 amp, 4 hours
		LPP	0 3	0 00	4100.20					4822 48			
		SPP	0.0	0.00	4100.14					4822 57			
		SPP	0.1	0 00	4100 47								
30	11	LNF	Alk.		[4105.35]	4105 16	0_9	31	0.1081054	4828 55	4828 44	1_7	Absolute experiment, current became unsteady during an electrical storm of unusual violence, 1/4 amp., 4 hours. Two large cups alkaline, omit these.
		LPP	Alk	.	[4105 24]					4828.36			
		SPP	0.5	0.01	4105.17					4828 40			
		SPP	0 1	0 02	4105.15								

[1] The forms used were the large non-septum form (LNF, Smith's new type), the large porous pot (LPP) and the small porous pot (SPP) types

TABLE III.—SUMMARY OF RESULTS.

No of run.	Mean silver deposit. Mg.	Mean iodine deposit. Mg.	Calculated coulombs: From Ag. coulometer.	Calculated coulombs: From cell and resis.	Calculated coulombs: Diff. Pts. in 10^6.	Weight.	Ratio silver : iodine.	Electrochemical equivalent of iodine.	Value of Faraday (I = 126.92).
2	4105.82	4829.59	3672.47	...	...	1.3	0.85013_8	1.31508	96,511
3	4104.69	4828.62	3671.45	3671.53	-2_2	3.0	0.85007_5	1.31518	96,504
4	4099.03	4822.24	3666.39	3666.55	-4_4	25.0	0.85002_6	1.31526	96,498
5^1	4397.11	5172.73	3933.01	...	..	22.2	0.85005_6	1.31521	96,502
6	4105.23	4828.51	3671.94	3671.84	$+2_7$	24.4	0.85020_6	1.31498	96,518
7^1	4123.10	4849.42	3687.92	...	..	16.2	0.85022_4	1.31495	96,521
8	4104.75	4828.60	3671.51	3671.61	-2_7	20.0	0.85009_1	1.31515	96,506
9^1	4184.24	4921.30	3742.61	...	.	20.8	0.85023_0	1.31494	96,521
10	4100.27	4822.47	3667.50	3667.65	-4_1	45.5	0.85024_2	1.31492	96,523
11	4105.16	4828.44	3671.88	3671.82	$+1_6$	100.0	0.85020_4	1.31498	96,519
Arithmetical mean (Nos. 4–11)........							0.85016	1.31505	96,514
Weighted mean (all observations)..... . . .							0.85017	1.31502	96,515

made. These also are international unit coulombs since they have been computed on the basis of the Weston normal cell taken as 1.0183 volts at 20° and the international ohm. The differences between these are given in the next column. On the average, the coulombs calculated from the coulometer are 1.5/100,000 smaller than from the measurements of current and time. This is as it should be, since the coulometer measurements at the Bureau of Standards recently have given a value for the cell about 2 or 3 parts in 100,000 lower than the adopted value 1.0183. The slight ambiguity that arises in the term "international coulombs" due to the possibility of measuring them in terms of the silver coulometer and time, or in terms of the international ohm, volt and time is fully explained in Part IV of the series of papers by Rosa, Vinal and McDaniel.[2] For the present purposes this difference is immaterial because, in computing the value of the Faraday, the international atomic weight for iodine is involved which is expressed only to five significant figures.

The system used in weighting the several experiments was purely mathematical, based upon the fact that for each result the error is due to the combination of experimental errors entering from the value of the factor for the arsenious acid (z_1), from the titration of the iodine deposits (z_2), and finally from the determination of the silver (z_3). The final result Z is then a function of these three quantities, $Z = f(z_1 z_2 z_3)$.

We may easily compute the possible errors of each of these factors from the average deviation. If we designate them as r_1, r_2, r_3, the probable error, R, of the result of an experiment is given by

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[1] The current strength for these runs was 0.05 amp. For the others it was 0.25 amp.

[2] *Bull. Bur. Standards*, 10, 478 (1914).

$$R^2 = \left(\frac{\delta Z}{\delta z_1}\right)^2 r_1^2 + \left(\frac{\delta Z}{\delta z_2}\right)^2 r_2^2 + \left(\frac{\delta Z}{\delta z_3}\right)^2 r_3^2.$$

These calculations have been carried out and weights computed inversely as the square of the probable error. Some system of weighting seemed to be necessary since the later experiments were deemed more reliable than the earlier ones. The experiments numbered 2 and 3 have small weights owing to the difficulties in weighing out the arsenious acid at this time so that they may practically be disregarded. We give also the arithmetical mean of Experiments 4 to 11 for comparison with the weighted mean. The two means are practically the same.

IV. Discussion of Results.

A. The Silver-iodine Ratio.—In Table III the results of this investigation have been presented in three ways: (1) as the ratio of silver to iodine, obtained by dividing the mean silver deposit by the mean iodine deposit; (2) as the electrochemical equivalent of iodine, obtained by dividing the mean iodine deposit by the coulombs as calculated from the silver voltameters; and (3) as the value of the Faraday, calculated from the electrochemical equivalent of iodine and the international atomic weight (1914) of iodine, 126.92. The ratio has been given chiefly because it possesses certain advantages for discussing the results. If the increase in weight of the platinum bowls used as cathodes represented only the weight of silver electrolytically changed from the simple Ag + ions to metallic silver, and if the only reaction taking place at the anode of the iodine voltameter is the formation of iodine from iodide ions under the action of the current, then according to Faraday's law the amounts of silver and of iodine so formed are in the ratio of the atomic weights of the elements.

Baxter,[1] who has made a very careful study of the atomic weights of silver and of iodine, as the result of early work gave 0.849997 as the value of this ratio. As a result of further work he arrived at the result 0.849930,[2] and more recently from a series of very concordant experiments he found the value 0.849906.[3] That calculated from the international atomic weights (1914) for silver and iodine, which are largely founded on Baxter's results, is 0.84998. The only other investigation of recent years which is comparable with the results of Baxter is that of Köthner and Aeuer[4] who determined the silver iodide : silver chloride ratio in eight closely agreeing analyses. Their result, on the basis of chlorine 35.457, gives 0.850013 as the value of the silver iodine ratio.

It is not our purpose to discuss these atomic weight determinations.

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[1] *Publ. Carnegie Inst.*, 135, 101.

[2] *Ibid.*, p. 108.

[3] This Journal, 32, 1591 (1910)

[4] *Ann.*, 337, 123, 362 (1904).

It is evident that our result, expressed as a silver-iodine ratio, is from 0.015 to 0.030% higher than that calculated from purely chemical methods. It seems unlikely that further work employing the same chemical reactions as have been hitherto used would cause this discrepancy to disappear, although Baxter considers that further evidence upon the silver-iodine ratio is desirable.

Our consistently higher results are in the direction of too heavy a deposit of silver or the formation of an insufficient amount of iodine. It may readily be suggested that the difference may be in part accounted for by inclusions of liquid in the silver deposit, but the conflicting results of previous observers do not permit us to estimate the amount. The last work by Laird and Hulett[1] indicated that deposits from pure solution probably do not contain more than 0.005% inclusions. The whole question of inclusions has been critically discussed by Rosa, Vinal and McDaniel.[2] Their opinion is that the deposits so perfectly crystalline as those formed from the purest silver nitrate do not contain significant inclusions. It is hoped that the work being carried out on this important subject in several laboratories will definitely settle the matter shortly. Until then the application of an inclusion correction to the value of the Faraday calculated from the silver coulometer can not be made with any degree of accuracy.

In connection with the iodine coulometer three possible sources of error suggest themselves. *First*, the main reaction which takes place at the anode resulting in the formation of iodine from iodide ions may have been accompanied by another electrochemical reaction, such as the formation of oxygen, which then remained dissolved in the solution. *Second*, sufficient iodine may have been formed, but a slight amount of it reacted with the water or with the metal of the electrodes. *Third*, the iodine used to standardize the arsenious acid solution may not have been sufficiently pure.

In the first place there is no certain difference between the results obtained using the current strengths of 0.05 ampere and of 0.25 ampere. The arithmetic means differ by 0.002% while the weighted means differ in the opposite direction by 0.003%. This shows that there is no appreciable error arising from such a reaction as the electrolytic formation of oxygen, for such a reaction would evidently be much greater with the higher current densities.

Secondly, had any of the iodine been lost by reacting with the platinum-iridium electrodes, this fact would have been immediately noticed, for it was found in the previous investigation that the presence of the slightest trace of platinum—less even than that corresponding to a loss of 0.001%

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[1] *Trans. Am. Electrochem. Soc.*, 22, 345 (1912).

[2] *Bull Bur. Standards*, 10, 516 (1914)

iodine—so affected the color of the solution that the end point in the titration was quite uncertain.

All of the iodine solutions which were employed in this investigation contained in addition potassium iodide. In such solutions the iodine exists in a large measure as the triiodide ion, I_3^-. Iodine may react with water in two ways; these may be conveniently expressed in the ionic forms,

$$OH^- + I_3^- = HIO + 2I^-$$

and

$$6OH^- + 3I_3^- = IO_3^- + 8I^- + 3H_2O.$$

The equilibrium constants of both of these reactions have been calculated.[1] By decreasing the concentration of the hydroxyl ion sufficiently, it is evidently possible to prevent the reaction of, and hence the loss of, any appreciable amount of iodine. The concentration of the hydroxyl ion in the solutions which were analyzed for iodine was so regulated by means of the addition of disodium phosphate that the loss of iodine due to either or both of the above reactions was less than 0.001%.[2]

The best evidence that the combined effect of errors due to the formation of electrolytic oxygen and to the loss of iodine through side reactions is negligible was obtained in the previous investigation on the iodine coulometer. The reaction which takes place at the cathode of the coulometers, is the formation of iodide ions from iodine, being just the reverse of that occurring at the anode. Hence in order to determine the silver-iodine ratio, or to calculate the Faraday, it is just as feasible theoretically to employ the amount of iodine used up at the cathode as it is to employ the amount formed at the anode. In the previous investigation both of these amounts of iodine were determined and it was found that they agreed with one another within the experimental error of 0.003%. That is, within this limit no side reactions, resulting in the formation of too little iodine at the anode, occur; the reaction taking place at the electrodes is strictly reversible. The amount of iodine used up at the cathode was not determined in the present investigation because the analysis of the cathode solution is much more difficult experimentally than is that of the solution at the anode.

Thirdly, if any of this discrepancy between the silver iodine ratios is to be ascribed to impurity in the iodine, this impurity would have had to consist of some oxidizing substance having a smaller equivalent weight than has iodine. The presence of an inert substance such as moisture would have caused a deviation in a direction opposite to that actually found. Special precautions were taken to eliminate from the iodine any oxidizing substance such as bromine. As described above the iodine was precipitated by means of potassium permanganate from a solution containing an excess of potassium iodide. The partly dried iodine was then distilled from a retort and caught in a molten condition, and finally it was repeatedly sublimed in a current of dry air. Any one of these three procedures should have practically eliminated any trace of chlorine or bromine which might have been present. The last step, the fractional sublimation, was carried through each time the arsenious acid solution was standardized. The procedure was not always the same, occasionally but three sublimations were employed, but more often five or six. It is scarcely possible that under such circumstances an amount of volatile impurity sufficient to account for an appreciable part of the discrepancy (0.015 to 0.03%) should have remained so constant in amount that the average deviations of the standardizations (see Table I) were but 0.0012%—an amount easily accounted for by experimental error.

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[1] Washburn, This Journal, 30, 31 (1908).

[2] This Journal, 34, 1352 (1912).

Taking these various sources of error into consideration, it is probable that the amount of iodine calculated to have been found at the anode is within 0.005% of that corresponding to the electrochemical change of iodide ions to iodine. The calculations of the value of the Faraday from this involves the atomic weight of iodine and the electrical measurements of the present investigation. It seems unlikely that the mean value for the Faraday (96.514 international coulombs) given in Table III is in error by more than 0.015%.

The possibility of electrical leakage on the coulometer stands being a source of error was also considered, but tests easily made showed the insulation to be ample.

B. The Faraday.—If the increase in weight of the platinum bowls of the silver coulometer be assumed to represent only the metallic silver formed from silver ions, then taking the atomic weight of silver as 107.88 the Faraday is equal to 107.88/0.00111800 or 96,494 international coulombs. From the iodine voltameter we obtained the value 96,514, the mean 96,504 probably represents within 0.01% the true value in international units.

Value in Absolute Units.—For theoretical purposes it is desirable that the value of the Faraday should be known in absolute units. We do not, however, think it advisable to emphasize this value at the present time for the following reasons: (1) Electrical measurements are almost universally made at the present time in terms of the international units as maintained by the several national laboratories. (2) Recent absolute measurements of the electrochemical equivalent of silver made in several countries differ somewhat among themselves and, therefore, it is necessary to state explicitly what is the basis of any computations that one might make. This is not the case with the international units. (3) It is probable that the difference between the absolute electrochemical equivalent of silver and the value 1.11800 adopted for the basis of the international ampere is as small as the uncertainties in the atomic weights of silver and iodine which are involved in the computation of the Faraday.

A recent investigation at the Bureau has given for the electrochemical equivalent of silver 1.11804 mg. per absolute coulomb. Hence, the absolute coulomb is 0.004% greater than the international coulomb, or the Faraday in absolute units is less by this amount. In absolute units the rounded off figure 96,500 seems the best value to assign, for the present, to this constant.

V. Comparison with Previous Investigations.

A. Silver Coulometer.—The present results with the silver coulometer are most easily compared with past work by considering the values computed for the Weston cell at 20° for the experiments in which the current was controlled. These experiments are called "absolute experiments" in Table II. In Table III we gave the coulombs as calculated from the silver deposits and also from the measured current and time. We noted in the discussion of this table that the first method gave a lower value on the average than the second by 1.5/100,000 which is significant of the difference between the exact value for the cell 1.01827 recently found by the voltameter and the figure adopted for use by the International Committee, 1.0183 volts. It is evident, then, that the present work has given 1.01828_5 for the cell value. This is perhaps more readily seen by computing the cell value for each silver deposit in an absolute experiment and taking the mean. Having done this we find the average value from Smith's new form of coulometer to be 1.01828_9 and from the porous cup coulometer to be 1.01828_0 whence the result 1.01828_5 as given above. The value 1.01827 given as the result of previous work is based on 211 deposits made with the greatest care by Rosa, Vinal and McDaniel.[1] It thus appears that the present work agrees with the past to 0.0015%.

B. Iodine Coulometer.—In their investigation, Washburn and Bates made a preliminary comparison of the silver and iodine coulometers. The relation between their results and ours is more readily discussed in terms of the silver-iodine ratio than by means of the value for the Faraday calculated from the iodine coulometer. This is because their value for the Faraday involves Smith, Mather and Lowry's absolute determinations, using the filter paper coulometer. The results of W. & B. give for the silver iodine ratio the value 0.85045, which is 0.033% higher than that recorded here. This difference is due to the fact that following the specifications of Smith, Mather and Lowry, they employed the filter paper form of silver coulometer. Recent investigations at the Bureau of Standards have shown conclusively that deposits obtained in such a coulometer are too heavy, because of the action of the filter paper. Hence in order to compare the previously obtained ratio with that given here, it is necessary to compare the filter paper coulometer with those forms used in the present investigation.

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[1] *Bull. Bur. Standards,* 9, 493 (1913).

The silver coulometers we employed were of the porous cup and non-septum types. The electromotive force of the Weston normal cell at 20°, calculated from deposits made in such coulometers, is 1.01827[1] volts. If the filter paper form is used the value 1.01866[2] is obtained, that is, the deposit in such a coulometer is about 0.038% heavier than that obtained in the types used in the present investigation. Making this percentage correction to the silver-iodine ratio determined by Washburn and Bates, the value 0.85013 is obtained, which agrees within 0.005% with our final value. This agreement is probably in part accidental since the filter paper coulometer is, in the hands of various investigators, scarcely capable of such reproducibility, and since in the previous investigation an accuracy better than 0.02% was not claimed for the final value, which was founded on but four comparative runs. It does, however, confirm the belief that our results are not in error by more than 0.01%.

VI. Summary.

We have made a careful comparison of the silver and iodine coulometers using them in series, so that the deposits of silver and iodine should be strictly comparable. The best procedure learned from previous investigations has been followed in each case. Our results are as follows:

1. Ratio of silver to iodine	0.85017
2. Electrochemical equivalent of iodine	1.31502
3. Value of the Faraday (I = 126.92)	96,515
4. Value of the Faraday (Ag = 107.88)	96,494
5. Value recommended for general use	96,500

Nos. 2, 3 and 4 are calculated on the basis of the international ampere, using 1.11800 mg. per coulomb as the electrochemical equivalent of silver.

The preliminary work in connection with the above investigation was carried out at the University of Illinois in the fall and winter of 1912–13. It was the original intention to make a careful comparison of the silver and the iodine coulometers there, employing the Bureau of Standards type of silver coulometer. This would, however, have necessitated considerable labor in preparing materials and especially in acquiring the practice and technique necessary to insure an exact reproduction of the Bureau's coulometer and methods of manipulation. Clearly the most desirable method of conducting the final series of comparisons was to take advantage of the experience in the use of the silver coulometer which had been gained at the Bureau of Standards. On taking the matter up with Dr. Rosa of the Bureau an invitation was extended and was gladly accepted to carry out the final series of measurements in the laboratories of the Bureau. The authors wish to thank Professor Washburn of the University of Illinois, who first planned the above investigation, for suggestions which have contributed in a large measure toward the success of the work. We also thank the Director of the Bureau and Dr. Rosa for assisting in making the arrangements for completing this investigation and for making available for this determination the excellent facilities of the Bureau.

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[1] *Bull. Bur. Standards*, 10, 486 (1914).

[2] *Ibid.*, 9, 197 (1912).

URBANA, ILL.
WASHINGTON, D C

THE ELECTROLYTIC REDUCTION OF IRON FOR PERMANGANATE TITRATION.[1]

BY H. C. ALLEN.

Received September 2, 1913

The following work was undertaken to determine the possibility of utilizing the oxidation-reduction effect of the electric current in certain analytical operations where it is desired to quantitatively oxidize or reduce a substance before its titration with a standard solution. Numerous studies have been made of the proper conditions for the deposition of the various metals by the electric current and the oxidizing effect has been utilized in a number of cases, especially with sulfides, where, after oxidation, the substance is precipitated and determined gravimetrically. The oxidizing and reducing effect of the electric current has also claimed much attention in both the organic and inorganic fields and in many of these latter studies it has been common practice to follow the reactions and determine the quantities of substances formed by titrating with some suitable standard solution. However, these titrations have been made for the purpose of obtaining the current or energy efficiency of the processes and very little work has been done along the line of producing a quantitative yield of the substance, in a strict analytical sense, regardless of the electrical efficiency of the process.

The rotating electrode, when employed in oxidations or reductions, should make the electrolytic method, in some cases at least, a successful competitor of the chemical methods of producing the same results, since it is possible to reduce small quantities of iron, for example, in from five to fifteen minutes by means of a rotating cathode under proper conditions. Further, the method has many advantages over the usual chemical methods of reduction. Some advantages that are at once apparent are that there is no danger of getting an excess of the reducing agent into the solution which must later be removed, and no foreign material is necessarily introduced into the solution before the titration.

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[1] Presented at the Rochester meeting of the American Chemical Society, September, 1913.

It should also be possible to regulate the oxidation or reduction to a nicety, through variations in the overvoltage, by choosing suitable anodes or cathodes, as is frequently the case in commercial processes when the current efficiency and maximum yield are the main points to be considered.

Apparatus.—The apparatus used in the electrolytic reduction consisted of six rotating electrodes belted to a single countershaft which was driven by a small motor. Being only a slight modification of the machines used in a number of places it needs no special description.

The cathodes of the various metals were made by bending a piece of wire sharply back upon itself at a point about 3 cm. from one end, the other end of the wire being left long enough to attach to the rotator. A rectangular metal gauze was then placed between the two wires thus formed and the gauze was twisted around in the form of a spiral. By rotating this spiral in the proper direction a maximum stirring is obtained, and the "vortex" effect in the liquid, which would tend to draw air into the solution, is largely eliminated by rotating the electrode near one side of the vessel rather than in the center. The wire stem used was of the same metal as the gauze in each case.

The anode, when of the non-soluble type, was of platinum wire, made as small as possible to carry the current without interrupting A short piece of platinum wire was fastened to a larger copper wire and a glass tube slipped over this and sealed off around the platinum, leaving about two centimeters of the wire exposed, which served as anode while the copper wire was fastened to the electrode holder. When soluble anodes were used the metal and size are indicated in the data.

The current was regulated by the number of lamps in series with the cell and in addition a sliding resistance was used for fine adjustment, which enabled any desired current to be obtained.

An automatic pipet was used for measuring out the solutions and the constancy of the amount withdrawn was checked at frequent intervals by weighing the quantity delivered. The extreme variations in these weights showed that the pipet could be relied upon to within about 0.1%, which was as close as the work in hand demanded.

Government standardized burets of 50 cc. capacity were used, graduated to tenths, while the quantity of permanganate used in most cases, where the reduction was complete, was approximately 20 cc. For the smaller quantities of permanganate, 10 cc. standardized burets, graduated to 0.05 cc., were used for greater accuracy.

The vessel used in most of the work was a beaker without lip of about 250 cc. capacity. During the run it was covered with a close-fitting watch glass to prevent loss by splashing and evolution of gases. The cover glass contained three holes: one for each of the electrodes and one for a thermometer.

Chemicals.—Baker's special analyzed or C. P. chemicals were used throughout the work.

Method of Procedure.– The general method of procedure was simple and consisted in delivering the solution to be reduced from the pipet into a 250 cc. plain beaker, making it up to the given amount with distilled water, placing it on the electrolytic apparatus and making the run under the conditions noted. About 0.12 g. of iron was usually taken. Two or three times during the run the cover glass and electrodes were washed down into the beaker and finally at the completion of the run they were again washed down, after lowering the beaker. The titrations were usually made with 0.1 *N* potassium permanganate at the temperature of the solution at the completion of the run, except at the higher temperatures, when the solution was cooled somewhat before the titration.

Experimental Part.

The surface, form and rate of rotation of the cathode, the dilution of the solution and the current strength were studied, but need not be considered, since the results obtained are not especially significant. The general effect of altering any one of these variables is easy to predict, being due largely to the same factor: getting fresh material into the sphere of action.

Cathode Material.- The subject of cathode material was not extensively studied since the object of the work was the practical reduction of the iron, and a copper gauze serves the purpose well and is easy to obtain in gauze form and quite pure.

A few runs were made with the cathodes indicated below, all other conditions being kept constant. A platinum gauze cathode was first used and then the different metals were plated on this cathode and the runs repeated.

Anode· platinum wire Acid 0.6 cc. conc. H_2SO_4 Solution 175 cc. Current: 1.9 amperes. Temp.: 26°. Time: 3 minutes

Cathode	Pt	Cu	Ag	Zn
$KMnO_4$ used, cc.	17.66	20.73	21.21	21.40

The last three metals given will reduce the iron even in the absence of a current, and this may account for their greater reducing power. The difference in potential at which the hydrogen will be liberated in the different cases may also be a considerable factor.

Solution—Acidity.—The following runs were made to determine the rate at which the iron would be reduced under the conditions given.

The first three series were made with the concentrations of acid indicated in the data. The concentrated acid (sp. gr. 1.84) is given throughout the paper.

Acidity: 0.6 cc. H_2SO_4 per 175 cc. solution. Cathode: Pt gauze, 5 × 6 cm. Anode: Pt wire. Temp.: 25°. Current: 1.6 amperes.

Time, minutes	1/2	1	2	3	4	5	8	9	10
% Fe reduced	16.1	32.6	57.4	78.2	88.7	93.8	99.4	99.6	100*

Acidity: 10 cc. H_2SO_4. All other conditions same as above.

Time, minutes	1	5	10	15	20	10
Temperature	25°	25°	25°	25°	25°	87°
% Fe reduced	23.0	76.8	94.1	99.4	100*	100*

Acidity: 35 cc. H_2SO_4 per 175 cc. solution. All other conditions same as the above.

Time, minutes	3	10	20	6	11
Temperature	28°	29°	28°	87°	81°
Current, amperes	1.9	1.9	1.9	4.0	1.9
% Fe reduced	45.3	54.8	63.5	99.2	100*

*In each of these cases a trace of ferric iron was shown by thiocyanate. The permanganate used indicated 100% reduction, to within the limit of experimental error. No blanks were subtracted from the permanganate used in titrating.

The time for complete reduction is shown to be 10 minutes with 0.6 cc. acid present while with 10 cc. acid at room temperature, 20 minutes are required. This time is cut down to 10 minutes at 87°. When as much as 35 cc. acid are present at room temperature the reduction is so slow that at the end of 20 minutes only 63% of the iron is reduced. In this case also the iron was completely reduced in 11 minutes at a temperature of 81°.

Two runs were made at room temperature with this latter acidity: one with a copper gauze and the other with a platinum gauze cathode, and complete reduction was not obtained in 75 minutes although the current was increased to 3.9 amperes during the last 15 minutes. Estimating from the intensity of the color with thiocyanate, equilibrium seemed to have been reached and it is very probable that the iron cannot be completely reduced at the lower temperature with this concentration of acid present.

The probable cause is that the greater concentration of sulfate favors the formation of persulfate which oxidizes the iron as fast as it is reduced. The higher temperatures are known to be unfavorable to the formation of persulfate, which would account for the complete reduction at the higher temperatures noted above.

In the two runs above with the copper and platinum gauze cathodes a zinc rod was substituted for the platinum wire anode after 75 minutes. With the copper cathode the iron was completely reduced, as indicated by thiocyanate, in 7 minutes while with the platinum gauze this was accomplished in 18 minutes. From this it would seem that complete reduction with the greater acidity is not possible except at the higher temperatures or by the use of a soluble anode.

If the formation of persulfate is the chief factor in preventing complete reduction of the iron, it is evident that neutralizing the excess of acid will not entirely correct the difficulty, and this was found to be the case. The same quantity of acid as used above was neutralized with sodium hydroxide until the excess of acid was less than 1 cc. sulfuric acid per 175 cc. solution and complete reduction was not obtained in 45 minutes, though a current of 3.7 amperes was employed. In this case, also, the iron was completely reduced in a few minutes by substituting a zinc rod anode for the platinum wire.

The effect of chlorides in the solution is similar and it is impossible to get complete reduction with a platinum wire anode because of the liberated chlorine, while with a soluble anode the chlorides do not interfere unless the current density becomes so great that chlorine is liberated.

Temperature—Acidity.—A number of runs were made to compare the rate of reduction at different acidities by determining the amount of iron that would be reduced in a given time. A series of these runs was made at 26° and another series at 76°.

Temperature 26° Cathode Pt gauze, 5 × 6 cm. Anode Pt wire Solution 175 cc. Current 1.9 amperes Time 3 minutes Average r. p. m. 1300

Acid, cc.	0.6	5	10	25	30	35	40	45	50
% Fe reduced	77.0	71.0	69.4	67.0	64.5	45.3	21.6	11.4	00.0

Temperature 76° All other conditions as above

Acid, cc	0.6	10	20	30	40	50	60	75	100
% Fe reduced	96.5	90.9	88.6	85.0	77.5	65.3	37.5	31.7	00.1

The general effect of acidity on complete reduction has been discussed and the above data are in accord with what has been said.

The percentage of iron reduced falls off very rapidly at room temperature with a concentration of acid from 25 to 40 cc. per 175 cc of solution, which may be partially accounted for by the fact that this is about the acidity of maximum conductivity for sulfuric acid, and with the greater concentration of hydrogen ion present the hydrogen may be liberated in preference to the iron being reduced. However, this is not the principal factor in the rapid drop in the amount of iron reduced, as the following data with soluble anode show:

Anode: Amalgamated zinc rod 4 mm. in diameter, immersed 6.5 cm. into the solution. Cathode: Pt gauze, 5 × 6 cm Temp 22° Current 1.9 amperes Solution: 175 cc Time: 3 minutes.

Acid, cc.	0.6	1	2	5	10	20	35	50	75
% Fe reduced	62.3	62.2	66.9	64.3	60.5	56.6	50.2	43.2	38.0

In this case the hydrogen at the cathode may be supposed to be liberated under much the same circumstances as with the platinum anode, but the rapid falling off in the amount of iron reduced is almost entirely absent The difference in results obtained in the two series over this range of acidity must be largely due to the formation of persulfate at the anode, with the platinum wire, which is eliminated by the use of the soluble anode.

This view is strengthened by the fact that about this acidity is given by Richarz[1] as being best suited for a production of persulfate.

Temperature.—The effect of an increase of temperature in addition to what has already been given, is quite well shown in the two series of runs following:

Acidity: 0.6 cc. H_2SO_4 per 175 cc. solution. Cathode: Pt gauze. Anode: Pt wire. Current: 1.9 amp. Time: 3 min. Av. r. p. m.: 1400.

Temperature	1.5°	8.0°	24.0°	26.6°	49.0°	63.0°	87.0°
% Fe reduced	53.0	63.0	76.4	78.4	88 0	94.0	99.6

Acidity: 40 cc. H_2SO_4 per 175 cc. solution. All other conditions same as the above.

Temperature	13°	25°	58°	90°	100°
% Fe reduced	00.0	21.6	61.2	85.6	89.2

In all cases an increase in temperature gives an increase in reduction and the effect of too great acidity can be very largely overcome by increasing the temperature. The above data show that with 40 cc. acid present no reduction takes place at 13°, while some of the previous tests indicated that at room temperature no reduction takes place with 50 cc. acid present, and at 76° the acidity may be increased to 100 cc. before the reduction becomes zero.

Anodes.—The general use of soluble or insoluble anodes has already been discussed in connection with other variables, and here as in the case of cathodes there is no very wide latitude for choice from a practical standpoint. The platinum wire serves the purpose very well when an insoluble anode is desired, while the amalgamated zinc leaves little to be desired in the line of a soluble anode. Magnesium was tried, but, since the acid reacts so readily with it, the acidity must be controlled within much narrower limits than with zinc.

The platinum wire used in the regular runs was modified by using a larger glass tube and sealing it off at the upper end, thus leaving a bell-shaped covering around the anode. A hole was blown in the side of the glass tube above the surface of the liquid to allow the escape of the liberated oxygen without mixing with the solution. This arrangement, when used on the blanks under the same conditions as the regular platinum anode, gave a solution that required only about one-half the quantity of permanganate needed when the oxygen was liberated in the solution without any special precautions to remove it.

If a selective reduction were to be made, the choice of suitable anodes or cathodes would be an important factor, but this is not the case in the present work, and since zinc is easily obtained in a fairly pure state and the effect of impurities may be largely overcome by amalgamation, it would seem to be the most practical metal to use.

Blanks with Current.—The question of a blank determination in the runs with platinum anode is not so easily settled, since the nature of the process taking place makes it very certain that the conditions that obtain without the iron present would give no indication of what to expect when iron is present. The sulfuric acid solution and the platinum electrodes would produce persulfate at the anode and this would react with the water for the formation of hydrogen peroxide.[1] The oxygen liberated at the anode, or from the air might also react directly with the hydrogen liberated at the cathode for the formation of hydrogen peroxide. This hydrogen peroxide would reduce the permanganate. However, in the presence of ferrous iron under the conditions of study, it would not be expected that these substances could possibly be formed to anything like the extent that they might be in the absence of the iron, since the ferrous iron would be oxidized and again reduced until equilibrium was reached.

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[1] *Ann. d. Phys.*, 24, 183 (1885); 31, 912 (1887).

A number of runs were made on blanks and it was found that they could be made to reduce enough permanganate to indicate 6–8% of iron in the solutions as ordinarily used. This quantity was obtained by allowing the cathode to rotate near the surface of the solution and thus create a vortex which drew down considerable quantities of air into the solution. When the cathode was rotated beneath the solution, in such a manner that no air was drawn into the solution, the reduction of permanganate, for a run of the same duration, was only about one-half the above amount.

It is quite certain that with the iron in the solution no such uncertainty exists in the electrolytic reduction as the above blanks might indicate, since a great many runs were made for complete reduction under quite different conditions, as indicated throughout the paper, and the checks obtained were very satisfactory.

The following comparisons were made between the zinc and electrolytic reductions in this connection: Two zinc reductions required 17.55 and 17.56 cc. permanganate solution for titration after deducting 0.12 cc. for a blank run at the same time. Four electrolytic reductions made from the same solution at the same time required 17.56, 17.57, 17.57 and 17.59 cc., respectively, with no deduction for a blank. From this it would seem that no great error will be made if a correction for a blank is omitted in the electrolytic reduction with platinum electrodes. While the electrolytic seem to be slightly higher than the zinc reductions, a very faint coloration was produced in a thiocyanate solution in each case after the electrolytic reduction.

When a zinc anode is used the conditions are somewhat different so far as a blank is concerned. The first two runs tabulated below were obtained by reduction with metallic zinc and the others by electrolytic reduction with zinc anode under the conditions noted·

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[1] Richarz, *Loc cit.*

	Zinc reduction.		Electrolytic reduction.		
Time.	2 hrs.	2 hrs.	22 min.	22 min.	16 min.
Acid, cc.	7.5	7.5	5	3	1
Solution, cc.	175	175	175	175	175
Wt. Fe sol., taken	25.556	25.545	25.533	25.522	25.543
$KMnO_4$, cc. used	22 81	22.81	22.78	22.75	22.76
$KMnO_4$ less blank	22.70	22.70	22.72	22.69	22.70

A blank run with the zinc at the same time and under the same conditions as the above required 0.11 cc. permanganate.

The electrolytic blank which was run with a careful exclusion of air and on the whole was rather lower than a number of other blanks that were run, required 0.06 cc. This may account for the electrolytic runs averaging slightly higher than the zinc reductions. In these electrolytic runs the reduction was carried to a point where no color was obtained by the thiocyanate test.

Reduction with Metallic Zinc.—A number of reductions were made with metallic zinc to compare the effect of acidity with similar runs made electrolytically, and the results were interesting.

Double the quantities of material used in the electrolytic reductions were placed in a 500 cc. Erlenmeyer flask, 14 g. of zinc distributed evenly over the bottom, and at the times indicated in the table below, 50 cc. of this solution were removed with a pipet, filtered to remove the particles of zinc, and titrated. The solutions were diluted to 350 cc. and the portions removed should have required 6.75 cc. of permanganate if totally reduced.

350 cc. sol.	8.	20.	50.	70.	90.	120.	150.
Time. Min.				$KMnO_4$. Cc.			
4	0.58	0.95	1.46	1.79	1.75.	1.52	0.96
11	1.46	2.36	3.69	3.71	3.61	3.08	1.96
21	2.64	4.20	5.31	5.20	5.07	4.44	2.93
31	3.92	5.48	6.07	6.07	5.88	5.29	3.59
45	5.38	6.46	6.65	6.65	6.57	6.05	4.26
60	6.24	6.66	6.76	6.74	6.77	6.49	4.30

Of the zinc used not any passed through a 60-mesh per inch sieve, 0.3% through a 40-mesh, 85.5% through a 20-mesh, and all would pass a 10-mesh sieve.

It is interesting to note that the zinc reduces fastest when the concentration of acid is from 50 to 90 cc. per 350 cc. of the solution, and this is the concentration of acid at which the electrolytic reduction with non-soluble anode is falling off the most rapidly. This is also about the concentration of greatest conductivity for the acid. It is possible that the large concentration of hydrogen ions in the solution is instrumental in keeping the surface of the zinc clean and in the best condition for reducing the iron. This particular range of concentration in connection with the electrolytic reduction has already been discussed.

The results obtained in the zinc reduction do not seem to be in entire accord with the statement of Carnegie[1] that the more nearly neutral the solution the more rapid the reduction, though the conditions are not quite the same, since he used zinc dust.

The zinc dissolves much faster in a solution containing iron than in one that does not, other conditions being the same. Hence the practice of running a blank experiment, so often recommended, is of doubtful value unless a pure zinc is used or all the zinc is finally brought into solution. This may also cause an uncertainty in methods similar to the Jones reductor method, though there is no doubt that the use of amalgamated zinc under these conditions prevents most other substances that would interfere with the titration from going into solution. The claim is made by Müller and Wegelin[2] that, when amalgamated zinc is used, there is no danger of iron precipitating on the zinc, but this phase of the subject was not studied.

Reduction without Auxiliary Current.

The method finally chosen as most practical for the reduction of ferric to ferrous iron dispenses with an outside source of current. In the course of the experimental work done in studying this method some observations of interest were made. The idea of using a substance that it is wished to reduce as a depolarizer in a short-circuited cell was first suggested by Löb[3] in connection with certain organic compounds. At this time the full value of rotating one of the electrodes was not realized and consequently the reactions proposed required several hours for completion. Since these same reactions could be obtained much quicker by purely chemical means the method has been very little studied.

The principle involved is perhaps to be found in the Gladstone-Tribe couple, and also is suggested in the numerous recommendations found in the literature to bring the zinc used in the reduction in contact with platinum. That bringing the zinc in contact with platinum has any advantage is contradicted by Müller and Wegelin[4] and data are given to show that this does not hasten the reduction of the iron In the same paper it is recommended that the zinc be brought in contact with metallic copper or that a little copper sulfate be added to the solution to hasten reduction. The end in both cases is the same, since the copper from the copper sulfate solution would be deposited on the zinc and assist in the reduction.

In the present work the same apparatus was used as in the previous work, but no outside source of current was used. One of the electrodes was rotated and the electrolytic cell produced by the two different metals in the acid solution was short-circuited by closing the switch on top of the apparatus. The contact was lubricated with oil and graphite to insure the least possible external resistance.

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[1] *J. Chem. Soc.*, 53, 468 (1888).

[2] *Z. anal. Chem.*, 50, 615 (1911).

[3] *Ber.*, 29, 1390 (1896).

[4] *Loc. cit.*

The following are some preliminary runs that have considerable bearing on the course of the work and so are given at this place:

1. Open-circuited cell with rotating platinum gauze cathode and stationary zinc rod anode. Acid: 10 cc. sulfuric acid per 175 cc. solution Time: 3 minutes. Temp.: 37°. Average r. p. m.: 800.

Permanganate required for titration: 2.27 cc

2. All conditions same as above, but cell short-circuited.

Permanganate required for titration: 17.47 cc.

While the conditions, so far as bringing the zinc into contact with platinum, are not the same as in the paper cited above, the values show an enormous increase in the iron reduced when the zinc is in contact with platinum in this manner. In the first case, above, the only office of the platinum is to stir the solution while the zinc does the reducing, and with its already limited surface partially covered with the liberated hydrogen offers very poor conditions for the reduction of the iron.

When the platinum is brought into contact with the zinc the hydrogen is liberated from the platinum gauze with the large surface, and the greater part of the reduction takes place on this surface, either from the action of the liberated hydrogen or the electrolytic action. Whether the use of the platinum increases the rate of reduction or not is very likely a matter of relative surface and if the platinum has much less surface than the zinc it may be that the reduction will be less than without the platinum, since the reduction that takes place on the surface of the zinc itself is possibly diminished when this is brought into contact with platinum. In the case above the platinum serves to increase the active surface of the system as a whole, hence the increase in the amount of iron reduced.

3. With amalgamated copper gauze cathode, $4^1/_2 \times 20$ cm., and amalgamated zinc rod anode, closed-circuited cell and all other conditions the same as No. 1 above.

Time for complete reduction: 27 minutes.

4. With silver plated on copper gauze, all conditions same as No. 3.

Time for complete reduction: 11 minutes.

5. With pure copper gauze cathode, all conditions same as No. 3.

Time for complete reduction: 8 minutes.

It is not feasible to use an open circuit when a copper cathode is used, since the copper goes into solution and deposits on the zinc in a loosely adhering mass which washes off and interferes with the titration. It is possible to get considerably more than 100% reduction as indicated by the permanganate consumed, under these circumstances.

Since copper itself is a very good reducing agent for the iron it makes very little difference in the amount of iron reduced whether the circuit is open or closed, providing proper precautions are taken to prevent the presence of metallic copper during the titration.

In a dilute acid solution, with the circuit closed, the copper also goes into solution, much the same as with the open circuit, and offers the same disadvantages. When the concentration of acid becomes as much as 10 cc. conc. sulfuric acid per 175 cc. solution none of the copper goes into solution when the cell is short-circuited, and the zinc remains clean and bright

Amalgamated and Unamalgamated Zinc Anodes.—The following runs were made to determine the effect of amalgamating the anode in the short-circuited cell without external current: The average speed of rotation was about 600 r. p. m. and the other conditions were as given in the table.

Time, minutes	8	8	26	13*	11
Temperature	36°	36°	38°	38°	58°
Acid, cc.	10	10	10	10	10
Anode Zn rod	unamalg.	amalg.	amalg.	amalg.	amalg.
$KMnO_4$ soln used	23.82	23.83	23.78	0.09	23.85
Loss in wt., anode	0.3062	0.1048	0.1480	0.0404	.

*Blank run with careful exclusion of air.

From these data it will be seen that by the use of amalgamated anodes only about one-third as much zinc goes into solution as when the anodes are not amalgamated, which is a point to be considered when working with impure zinc. The efficiency of the amalgamated zinc is also remarkably high, approaching 70% for complete reduction of the iron, which is another important factor in the practical reduction of the iron when the quality of the zinc is uncertain. In an ordinary reduction with metallic zinc from 3 to 5 g. of the metal would be used, whereas in the present reduction only a little more than 0.10 g. of zinc went into solution. The efficiency of the zinc for a 95% reduction of the iron was made to reach as high as 96% in a number of runs.

In the above runs the solutions withdrawn by the pipet were not weighed, which may account for the rather wide variation in the results. Complete reduction was indicated in each case by sulfocyanate.

The 26-minute run was made to test the effect of running after all the iron was reduced, which was at the end of eight minutes.

The cathode in the above trials changed in weight only a few tenths of a milligram during the run.

Rate of Reduction.—The following runs were made to determine the rate of reduction in the short-circuited cell without external current:

Cathode: Cu gauze, $4^1/_2 \times 20$ cm. Anode: Amalg. Zn rod. Acid: 10 cc. H_2SO_4. Solution: 175 cc. Temp. · 37°.

Time, minutes	$^1/_2$	1	2	3	5	8
% Fe reduced	43.2	64.1	87.0	91.7	97.9	100

This series of results shows the same general characteristics as that obtained with current and needs no comment, except perhaps to note that the iron is completely reduced in less time in this case than when a current of 1.6 amperes is employed, but this may be wholly or in part due to the fact that a larger cathode was used or the temperature of the solution was a little higher.

Blanks without Current.—Blanks run without current could be made to consume from 0.06 cc. to 6 or 7 cc. of permanganate and are no doubt worthless, probably due to the formation of hydrogen peroxide in the solution from the oxygen dissolved in the solution or from the oxygen of the air. This hydrogen peroxide could not exist in the ferrous solution and since so little zinc goes into solution during the reduction it would seem that the blank should be only that quantity of permanganate that is necessary to give the end color in a solution of the same volume, containing a like quantity of acid and iron in the ferric condition, as the iron solution to be determined. In a blank, run with the careful exclusion of air, about the same quantity of permanganate will be consumed as the excess used when ferric iron is present but this is not due to impurities in the zinc and is only an accidental agreement. These same conditions may also apply to a certain extent to any of the methods of reduction where metallic zinc is used.

Blackening of Cathode.—When using a copper cathode it was noticed that in some cases the copper would become quite black while in others it would remain bright. A few qualitative runs were made to determine the conditions that favored the blackening. This blackening did not seem to interfere with the accuracy of the determination except in a few cases with low acidity and large current, when it was evidently partly due to iron being deposited on the cathode.

Among the conditions that were found to favor the blackening were the following: (1) low acidity; (2) small zinc surface in the short-circuited cell; (or 3) comparatively large copper surface; (4) large iron concentration; (5) presence of chlorides; (6) low current density when current was employed.

Finally, as a general check on the reductions, double the quantity of solution used in the previous trials was weighed out and reduced under the conditions given below: It is believed that the results indicate about the accuracy to be obtained by the method when considerable care is used.

Time, minutes................	*	30	30	30
Acid, cc.....................	.....	2	5	15
Anode........................	.....	Pt wire	Amalg. Zn	Amalg. Zn
Cathode......................	.. ..	Pt gauze	Pt gauze	Cu gauze
Current amp..................	.....	1.9	1.6	0.0
Blank, cc....................	0.17	0.00	0.13	0.13
Fe per g. of solution...	0.005447	0.005448	0.005448	0.005445

*Jones reductor.

The Crescent iron ore, put out by the Bureau of Standards, gave the following results:

Time, minutes	30	30	30	45	30
Acid, cc. H_2SO_4	5	10	10	20	15
Anode	Pt wire	Amalg. Zn	Amalg. Zn	Amalg. Zn	Amalg. Zn
Cathode	Pt gauze	Pt gauze	Cu gauze	Cu gauze	Cu gauze
Current, amp.	2.2	1.9	1.6	0.0	0.0
Blank, cc.	0.0	0.13	0.13	0.13	0.13
% Fe	58.70	58.66	58.70	58.77	58.70

In the preliminary treatment of the ore, the recommendations of the Bureau were followed and the permanganate used in the titrations was standardized by sodium oxalate obtained from the Bureau of Standards. No correction has been applied for the small amount of titanium (0.07% TiO_2) present in the ore which may account for the values being higher than the value of 58.62% given by the Bureau of Standards.

Conclusions.

1. It is possible to get practically complete reduction of ferric iron, as indicated by permanganate consumed, by using a large platinum cathode and small platinum wire anode if the concentration of sulfate is small. No blank should be subtracted.

2. By using a soluble anode and platinum cathode, complete reduction is possible with wide range of acidity, but with low acidity some of the iron may be deposited on the cathode with high current density.

3. Chlorides must be absent with platinum anode, but with soluble anode may be present unless too great current density is employed.

4. By using a short-circuited cell with platinum gauze cathode and zinc anode, complete reduction may be obtained with wide range of acidity.

5. The most practical method of reduction in most cases is a short-circuited cell with copper gauze cathode and amalgamated zinc rod anode. The concentration of acid must be at least 10 cc. conc. H_2SO_4 per 175 cc. solution. Under these conditions 0.12 g. of iron may be reduced at room temperature in eight minutes with a zinc efficiency of 70%.

6. With short-circuited cell, chlorides do not interfere with the reduction.

7. Increase in temperature in every case increases the rate of reduction.

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NOTE.

A Thermo-Regulator for Electrically Regulated Constant Temperature Chambers.[1]—The need for an adjustable thermo-regulator for electrically controlled constant temperature chambers of any description has led the writers to devise the form represented in the accompanying illustration, Fig. 1. Regulators of this type which have been in use for some time have proved so satisfactory that it seems worth while to publish a brief description of the apparatus.

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[1] Published by permission of the Secretary of Agriculture.

This regulator consists of a main "bulb" whose form may be varied according to requirements, and a capillary stem provided with a small auxiliary bulb[1] *g* connected with the stem by a capillary neck. Platinum wires are sealed in at the points *d* and *d'*. The wire at *d* should barely protrude into the capillary, and an enlargement of the bore at that point should be carefully avoided. The stem of the regulator is graduated in millimeter units for a distance of one or two centimeters above and below the wire *d*. This graduation greatly facilitates the adjustment of the regulator. In the unsealed regulator the stem *i* should extend 15 to 20 cm beyond the auxiliary bulb

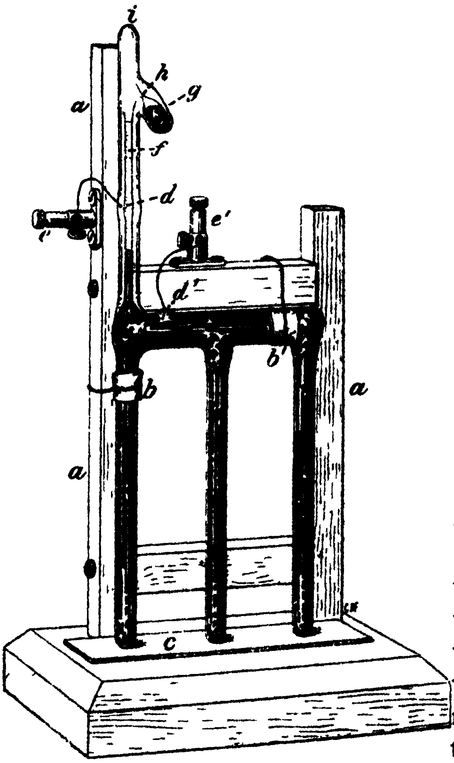

Fig 1.

The apparatus is filled in the following manner The capillary stem is connected with a vacuum pump by means of an intermediary three-way stopcock. When the air has been exhausted from the apparatus, mercury is allowed to run in until the bulb and part of the capillary stem have been filled. A little mercury is allowed to run into the auxiliary bulb also. The stopcock is then removed and the tube from the vacuum pump is attached directly to the stem of the regulator The tube should be firmly wired on. The regulator is suspended by means of this tube while the air is exhausted with a high vacuum pump. While thus evacuated the parts of the regulator are carefully heated section by section until all the mercury has been boiled. Mercury is now boiled over from the auxiliary bulb into the stem until the stem is completely filled to the neck of this bulb. Finally, the mercury in the auxiliary bulb is kept boiling under the low pressure while the stem is sealed off at *i*. In this way the air is entirely removed from the apparatus and corrosion of the mercury surface, due to sparking at the point of contact with the wire *d*, is obviated. In order to avoid sparking, the regulator should be used with a current of very low amperage (0.01 amp. or less) which actuates a relay. The heating current can not be passed through the apparatus.

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[1] A side-bulb resembling the one here described but connected with the stem by a wide neck has been described by Regaud and Fouilland for another form of regulator. *Ann. rev. chim. analyt*, 14, 141–146 (1909).

To adjust the regulator, a small quantity of mercury is shaken from the auxiliary bulb into the stem or from the stem into the bulb, according to whether adjustment for a lower or higher temperature is desired. The capillary connection *h* should be rather narrow, as otherwise it is not possible to transfer sufficiently small globules of mercury to effect an accurate adjustment. The adjustment is greatly facilitated by the graduation on the stem. When the regulator is brought to the desired temperature by means of a water bath, the number of graduations between the level of the mercury column and the wire *d* will indicate the quantity of mercury which must be transferred from the stem to the auxiliary bulb, or conversely. The transfer may be made after the regulator has returned to room temperature. The form of the main "bulb" of the regulator is, of course, immaterial and may be varied according to requirements. In the type illustrated, the bulb consists of a large tube 1 cm. in diameter with three small tubes each 10 cm. long. This form has been found very convenient where the regulator is placed directly in the chamber to be controlled. Where the temperature is indirectly controlled, as in the water jacketed incubators in common use in laboratories, an oblong bulb would be more convenient. In the regulator illustrated, the volume of the mercury up to point of contact *d* is about 20 cc. The increase in volume per degree would be 0.0036 cc. The diameter of the capillary *f* is about 0.16 cm. Its cross-section would, therefore, be 0.02 sq. cm. The linear expansion in the capillary per degree centigrade would be 0.18 cm. The length of the capillary is 5 cm., its volume 0.1 cc. This volume of mercury would correspond to the expansion of 20 cc. of mercury caused by a rise through 28°. The volume of the bulb *g* is about 0.5 cc., allowing a possible temperature range of over 100°.

[1] The apparatus was constructed for the writers by E. Machlett & Son, 153 East 84th St., New York, N. Y.

BUREAU OF PLANT INDUSTRY,
U S DEPT OF AGRICULTURE

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ON THE STEARATES AND PALMITATES OF THE HEAVY METALS WITH REMARKS CONCERNING INSTANTANEOUS PRECIPITATIONS IN INSULATING SOLUTIONS.

BY ALFRED E. KOENIG.

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Introduction.

The stearates and palmitates of the heavy metals have been known for a long time. Brief accounts of their preparation and analysis are found in Chevreul's "Les Corps Gras" and in Liebig's Annalen.[1] But little further work has been done on them.

Kahlenberg[2] has performed many experiments to show that all types of chemical reactions which take place in conducting solutions, and are attributed to the ionization of the compounds entering into the reaction, may be duplicated in non-conducting solutions. For these experiments it was necessary to employ organic solvents, and in most of these the stearates, palmitates, and oleates of the heavy metals dissolve. This is due to their high carbon content, as Kahlenberg has pointed out. The oleates have been most frequently used, but, since they are generally of a smeary consistency, they present many experimental difficulties. The stearates and palmitates of the heavy metals, because of their higher melting points, can readily be reduced to a powder and thoroughly dried. They therefore lend themselves much more satisfactorily to various purposes.

The work described in this paper was undertaken to investigate further the properties of the stearates and palmitates of the heavy metals and also the solutions of these salts.

Experimental.

Preparation of the Salts and Instantaneous Precipitations in Their Solutions.—Merck's palmitic and stearic acids were used in the preparation of the stearates and palmitates. The chlorides and sulfates of the heavy metals were also from the same source. The pyridine, benzene, toluene, carbon tetrachloride, and other solvents employed in this work, were of Merck's best grade.

The copper, cadmium, cobalt, chromium, iron, lead, manganese, mercury, nickel and zinc salts were prepared according to the following general method: About 15 g. of the sodium soap were dissolved in a liter of warm water. This always yielded a clear solution, whereas, if the soap was placed in cold water and then warmed, a cloudy liquid would be obtained. The clear liquid, prepared as just described, sets to a solid jelly if allowed to cool. The warm solution of the soap was poured into an excess of a 1% solution of the chloride or sulfate of the heavy metal, with vigorous stirring. The flocculent precipitate of the heavy metal soap was washed by decantation until the washings were found to be free from soluble salts. The stearates and palmitates were dried in an air bath at 115° to 120° for ten to twelve hours. The flat crystallizing dishes in which the salts were dried were so large that the resulting clear liquid, which in cooling solidified to a glassy solid, formed a layer not more than a millimeter thick. The salts were powdered and kept in glass stoppered bottles till used.

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[1] *Ann.*, **35**, 51 (1840); **36**, 44 (1840); **84**, 297 (1851), and **88**, 298 (1853).

[2] *J. Phys. Chem.*, **6**, 1 (1902).

For the preparation of the sodium soaps, a quantity of the fatty acid was added to *a little less than* its equivalent of $N/2$ NaOH solution in a flask provided with a reflux condenser, and was then heated on a steam bath for ten to twelve hours. The clear solution was filtered through cotton, which retained the small globules of uncombined acid. This procedure is quite essential to avoid the formation of basic salts, when the heavy metal salts are precipitated by means of the sodium soaps. Cady[1] in a recent article, states that when a dehydrated solution of copper oleate in benzene and one of hydrochloric acid in benzene, both of which have an extremely low conductivity, are mixed there results an instantaneous precipitation of copper chloride, accompanied by a large increase in the conductivity of the resulting solution. This latter phenomenon is contrary to that observed by Kahlenberg.[2] The increased conductivity, observed by Cady, may be due to the different manner of preparing the copper oleate. In Cady's method, oleic acid was neutralized with an *excess* of sodium hydroxide. When this sodium oleate solution is used for the precipitation of copper oleate, a basic copper oleate is necessarily formed. The reaction of the basic oleate with hydrochloric acid would result in the formation of a certain amount of water which with the hydrochloric acid present would cause an increase in the conductivity of the solution.

Kahlenberg[2] has pointed out that many reactions of the type of double decompositions take place as readily in non-aqueous solvents as in water. I found that such a reaction occurred when a solution of cupric stearate in benzene was brought together with a solution of stannic chloride in the same solvent. An *instantaneous* precipitate of cupric chloride was formed. The clear filtrate was heated on a water bath to distil off the excess of stannic chloride and the benzene. A light yellow liquid remained in the retort which solidified at about 50°. On analysis this yielded 15.06% of stannic oxide and the results of three analyses, one of which was of a sample prepared at a different time, checked very closely. This would indicate a basic stannic stearate of the formula $Sn(C_{17}H_{35}COO)_4.SnO(C_{17}H_{35}COO)_2$. Likewise a benzene solution of silicon tetrachloride run into a benzene solution of cupric palmitate formed an instantaneous precipitate of cupric chloride. The colorless filtrate on evaporation at room temperature left a gelatin-like solid which charred only slightly on ignition, and yielded 82.3% of SiO_2. This would show that if a silicon palmitate was formed at all, it was a basic salt as might be expected, but the matter was not investigated any further.

The fact that instantaneous precipitation of cupric chloride thus occurs in benzene solutions of cupric stearate and cupric palmitate shows conclusively that such phenomena are not due to the unsaturated condition of the acid radical, for the stearic and palmitic acids are saturated compounds. This then conclusively refutes Cady's[1] claim that the unsaturated condition of the oleates is the cause for similar instantaneous precipitations in their solutions.

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[1] This Journal, **35**, 1434 (1913).

[2] *J. Phys. Chem.*, **6**, 1 (1902).

Solubilities.—To determine the qualitative solubility of the salts that were prepared, a portion of the finely powdered salt was placed in a test tube and shaken with a few cubic centimeters of the solvent. After standing for several hours, a portion of the liquid was evaporated on a watch glass. The solubility in the hot solvent was determined in the same way after the lightly corked test tube containing the salt and the liquid had been warmed on a steam bath for an hour. The results have been placed in Table I. In this table (S) indicates that the salt is soluble to the extent

Table I.

Solvent	Chromium stearate.	Copper stearate.	Copper palmitate.	Cobalt stearate.	Cobalt palmitate	Nickel stearate.	Manganese stearate.	Stannic stearate
Pyridine, cold	S	S	S	S	S	S	S	S
Pyridine, hot	S	S	S	S	S	S	S	S
Benzene, cold	I	I	I	s	s	S	I	s
Benzene, hot	s	S	S	S	S	S	s	S
Toluene, cold	I	I	I	s	s	S	s	S
Toluene, hot	s	S	S	S	S	S	S	S
Carbon bisulfide, cold	s	I	I	s	s	S	s	S
Carbon bisulfide, hot	S	S	S	s	s	S	s	S
Chloroform, cold	s	s	s	S	S	S	I	S
Chloroform, hot	S	S	S	S	S	S	I	S
Carbon tetrachloride, cold	s	s	s	S	S	S	I	S
Carbon tetrachloride, hot	S	S	S	S	S	S	I	S
Amyl alcohol, cold	I	S	S	S	S	S	I	S
Amyl alcohol, hot	I	S	S	S	S	S	I	S
Methyl alcohol, cold	I	I	I	I	I	I	I	S
Methyl alcohol, hot	I	I	I	I	I	s	I	S
Ether, cold	I	I	I	s	s	I	I	—
Ether, hot	I	I	I	s	s	S	I	—
Acetone, cold	s	I	I	I	I	I	I	S
Acetone, hot	s	I	I	I	I	s	I	S
Ethyl acetate, cold	s	s	s	I	I	I	I	—
Ethyl acetate, hot	s	S	S	I	I	I	I	—
Paraffin, cold	S	S	S	S	S	S	S	S
Paraffin, hot	S	S	S	S	S	S	S	S
Heptane, cold	I	s	s	s	s	s	I	I
Heptane, hot	I	S	S	S	S	S	I	s

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[1] *Loc. cit.*

of about 1% or more; (s) indicates that only a few hundredths of a % dissolved, and (I) that the salt is insoluble.

As Table I shows, the cobalt, copper, and nickel stearates and palmitates were insoluble, or only slightly soluble, in cold benzene, toluene, heptane, chloroform, and carbon tetrachloride. When warmed for some time with these liquids, 1–2% solutions may be obtained. From solutions in these solvents, the salts did not separate on cooling. The whole liquid always set to a homogeneous jelly. Thus a 1% solution of stannic stearate in methyl alcohol yielded a jelly, showing that this salt behaves like the stearates of the other heavy metals. Kahlenberg[1] has shown that copper oleate is soluble in cold benzene. Since the copper salts of stearic and palmitic acids were found to be insoluble in this solvent, these facts might be used to separate these acids from oleic acid.

All the stearates and palmitates were found to be copiously soluble in hot pyridine. Some of these hot saturated solutions on cooling deposited distinctly crystalline addition products of the heavy metal soaps with pyridine. A hot saturated solution of copper stearate, or palmitate, was of a deep bluish green color which turned to a deep blue on cooling and yielded a crop of green rectangular plates or granular masses. The mother liquor on standing deposited deep blue, feathery crystals in radiating clusters. A solution partly saturated at 80°, and allowed to cool very slowly, solidified almost entirely to a mass of light blue needles. The green crystals were quite stable and did not effloresce on exposure to the air for several weeks. They were found to contain one molecule of the copper soap combined with one of pyridine ($Cu(C_{17}H_{35}COO)_2.C_5H_5N$ and $Cu(C_{15}H_{31}COO)_2.C_5H_5N$. The deep blue crystals were fairly stable but changed to an amorphous powder on exposure to the air. They were found to contain two molecules of pyridine to one of the soap. The light blue needles, when placed on a porous plate, quickly lost their pyridine and with it their crystalline form. Their composition has not been ascertained.

A hot, saturated solution of the stearate or palmitate, of cobalt was a deep red color. This on cooling yielded rose colored plates which were found to contain two molecules of the pyridine to one of the cobalt salt. The crystals effloresced slowly to a pink amorphous powder.

The hot, saturated solution of the nickel stearate has a light green color similar to that of an aqueous solution of nickel chloride. This solution yielded green crystalline plates that appeared a bluish green when the excess of mother liquor had drained off. These crystals were stable, and were found to contain two molecules of pyridine to one of the stearate.

All of these crystalline products have a well defined melting point, whereas the soaps themselves do not, as is shown by the following table·

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[1] *J. Phys. Chem.*, 6, 1 (1902)

TABLE II.—THE MELTING POINTS OF THE PURE SOAPS AND OF THEIR CRYSTALLINE COMPOUNDS WITH PYRIDINE.

Soaps.	M. p.	Crystalline products.	M. p.
Copper stearate	115–125°	$Cu(C_{17}H_{35}COO)_2.C_5H_5N$	87.0°
Copper palmitate	115–120°	$Cu(C_{15}H_{31}COO)_2.C_5H_5N$	86.6°
Cobalt stearate	73– 75°	$Co(C_{17}H_{35}COO)_2.2C_5H_5N$	70.4°
Cobalt palmitate	70– 75°	$Co(C_{15}H_{31}COO)_2.2C_5H_5N$	64.0°
Nickel stearate	80– 86°	$Ni(C_{17}H_{35}COO)_2.2C_5H_5N$	85.4°

After having obtained several crops of crystals from the solution of the copper soap, the remaining liquid no longer had the same color as a fresh solution but became a dark green. It then deposited a light blue crystalline crust, together with a brownish slimy precipitate. The solutions of the cobalt soaps became a reddish brown and deposited a pink crust mingled with a brown precipitate. It is evident that this method of crystallization might be used to prepare the pure stearates and palmitates. The salts obtained by heating the addition products to constant weight, at a temperature high enough to drive off the pyridine, were found to contain the theoretical proportion of the heavy metal.

From hot solutions of the stearates of lead, chromium, trivalent iron, cadmium, manganese, mercury, and zinc, on cooling or evaporating the solvent, these salts separated out as a sticky amorphous mass. This loses its adherent pyridine and becomes a hard glassy solid like the original salt.

Förster[1] obtained bright green crystalline plates of $Cu(C_2H_3O_2)_2.C_5H_5N$ and deep blue needles of $Cu(C_2H_3O_2)_2.4C_5H_5N$ from aqueous solutions of the acetates with pyridine. Grossman and Hünseler[2] obtained dark blue plates of $Cu(C_2H_3O_2)_2.2C_5H_5N$. These crystals in their appearance and composition were analogous to the compounds of the stearates and palmitates of copper with pyridine. Senbert and Rauter[3] describe crystals, of similar appearance and composition, of copper oxalate with pyridine. Grossman and Jäger[4] also describe red crystalline plates of the oxalates, acetates, formates and tartrates of cobalt, each with two molecules of pyridine to a molecule of the salt, and green crystals of nickel acetate with two molecules of pyridine. These are also analogous to the corresponding stearates and palmitates. The last investigators found similar addition products with the acetates and formates of such bivalent metals as manganese, mercury, cadmium, and zinc. Aside from a kind of crystalline crust and spherical nodules, no definite crystalline product with the stearates of these metals was formed. Lutschak[5] gives many analogous addition products of salts of the heavy metals with ammonia.

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[1] *Ber.*, **25**, 3416 (1892).

[2] *Z. anorg. Chem.*, **46**, 301 (1905).

[3] *Ber.*, **25**, 2823 (1892).

[4] *Z. anorg. Chem.*, **48**, 73 (1906).

[5] *Ber*, **5**, 30 (1872).

Saturated solutions of copper and cobalt stearates in quinoline, amylacetate, and benzaldehyde were prepared at about 70° and allowed to cool. The quinoline and benzaldehyde solutions apparently yielded crystals. As there was evident decomposition, shown by the blackening of the solution, these crystals were not investigated further. With amyl acetate the copper stearate swells up to more than four times its original volume and forms light blue granules which contain over half their weight of amylacetate.

The stearates of nickel, cobalt, copper and chromium dissolved readily in melted stearic acid and paraffin. Uniform solids were formed on cooling. Apparently no addition product separated out. With a view to making a double sodium copper salt, the copper stearate was heated for a long time in a concentrated aqueous solution of sodium stearate. The copper stearate remained unchanged. The treatment of the copper soap with an alcoholic solution of sodium stearate resulted in no apparent change in the copper stearate.

To determine the composition of the crystalline addition products, the crystals were formed in crystallizing dishes. The pyridine was drained off, the crystals thrown upon filter paper, and dried as quickly as possible. Portions for analysis were placed in crucibles and weighed. The samples were heated in an air bath at 115 to 120° to constant weight and the pyridine determined by the loss in weight. The crucibles were then placed on a sand bath and so heated that the organic matter was charred and gradually oxidized. To insure the complete oxidation of the organic radical, the contents of the crucibles were treated with a quantity of finely powdered ammonium nitrate and finally a few drops of nitric acid. The copper and nickel were determined as the oxides. The cobalt was converted into the sulfate and weighed as such. Each of the results given in Table III is the average of two or three analyses.

It has been noted by Kahlenberg that cobalt oleate, dissolved in xylene, changes from pink to blue on heating. A number of such color changes in the solutions of the stearates and palmitates was noted. A solution of cobalt stearate in Merck's paraffin, m. p. about 60° was brown when cold. It melted to a straw colored liquid, became pink, and finally was a deep blue at about 180°. Cobalt stearate dissolved readily in melted stearic acid, palmitic acid, naphthalene, and phenol. These mixtures behaved in a manner similar to that of the paraffin solution. A dilute solution of the salt in benzene, carbon tetrachloride, or amyl alcohol solidified to a pink jelly which, on heating, melted and changed to lavender color and became a deep violet, when the liquid had reached its boiling point. The higher the boiling point of the solution, the more nearly blue the hot solution became. Cobalt palmitate was found to behave in the same manner as the stearate in all these solvents. In all cases the solutions became pink on cooling and blue on heating.

TABLE III.—RESULTS OF ANALYSES.

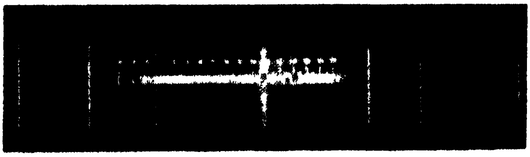
Blue crystals of copper stearate with pyridine.

	Copper oxide.	Pyridine.
Calc. for $Cu(C_{17}H_{35}COO)_2.2C_5H_5N$	10.10%	20.06%
Found	9.93%	21.92%
Green crytsals of copper stearate with pyridine.		
Calc. for $Cu(C_{17}H_{35}COO)_2.C_5H_5N$	11.14%	11.33%
Found	11.21%	11.27%
Green crystals of copper palmitate with pyridine.		
Calc. for $Cu(C_{15}H_{31}COO)_2.C_5H_5N$	12.12%	12.21%
Found	11.96%	12.13%
Red crystals of cobalt stearate with pyridine		
	Cobalt sulfate.	Pyridine.
Calc. for $Co(C_{17}H_{35}COO)_2.2C_5H_5N$	19.86%	20.18%
Found	19.96%	20.23%
Red crystals of cobalt palmitate with pyridine.		
Calc. for $Co(C_{15}H_{31}COO)_2.2C_5H_5N$	21.46%	21.74%
Found	21.72%	21.58%
Green crystals of nickel stearate with pyridine.		
	Nickel oxide	Pyridine.
Calc. for $Ni(C_{17}H_{35}COO)_2.2C_5H_5N$	10.21%	21.52%
Found	10.09%	21.57%

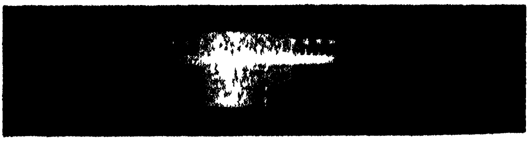
The red crystals of cobalt stearate and palmitate with pyridine melt and change to deep blue on heating to about 150°. On cooling they return to their original red color. The dry cobalt soap itself melted to a rose colored liquid which turned to blue on heating. Even after heating for several minutes over a bunsen flame, the salt would assume its rose color when it had cooled. The color change in these cobalt salts must consequently be due to some intramolecular change and can not be ascribed to hydration or ionization.

Copper stearate dissolved in hot paraffin or naphthalene gave a light yellow solution which formed a bright green solid on cooling to room temperature. The yellow color would return when it was melted and on solidifying the solid would again become bright green. Copper abietate behaves in a similar manner, and it has been noted in this laboratory that copper camphorate also showed this property. These changes are evidently analogous to those of the cobalt salts.

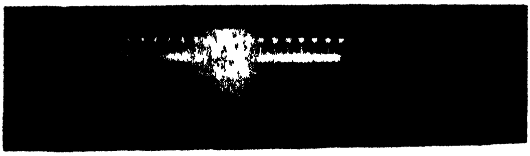
Absorption Spectra.—A half or quarter normal solution of the stearate was prepared and placed in a two-millimeter cell. The absorption spectrum of this solution was photographed. Five cubic centimeters of the solution were then diluted with an equal volume of the solvent. The absorption spectrum of this dilute solution was photographed. This method of procedure was continued until the spectra of six dilutions had been obtained. Thus the photographs of the pyridine and carbon tetrachloride solutions of the stearates of copper, cobalt, and nickel were obtained. These were compared with the photographs of the absorption spectra of aqueous solutions of the chlorides of the same metals made in the same way with the exception that the first solution was four times as strong. This strength was used because it takes an aqueous solution of



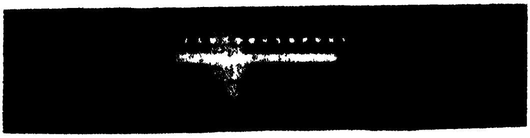
Helium spark spectrum



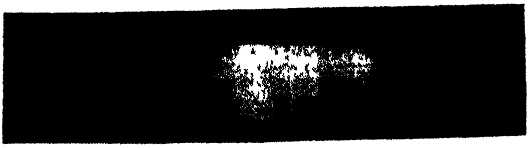
n solution of copper chloride in water



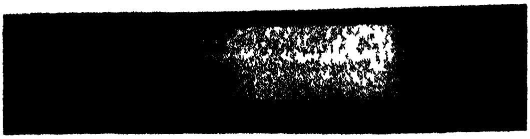
n 16 solution of copper stearate in pyridine.



n 16 solution of copper stearate in carbon tetrachloride.



n 2 solution of nickel chloride in water



n 16 solution of nickle stearate in pyridine

n 16 solution of nickel stearate in carbon tetrachloride.

about four times the concentration of the solution of the soap of the same metal to produce a liquid of the same intensity of color. Upon each spectrum photograph, there were also a scale and the sodium lines. To furnish a scale of reference, this same scale was photographed with the sodium lines and a spark spectrum of helium. The photographs were made by means of a Steinheil spectrometer with a Rowland grating. Cramer's Spectrum Plates were used and each was given the same time of exposure and development.

As far as this work was carried, there appeared no fundamental difference between the absorption spectra of the aqueous solutions of the salts of copper, cobalt, and nickel and those of the solutions of their stearates in non-aqueous solvents. The spectrum photographs have not all been included in this paper. However those given in Plate I, show that the insulating solutions of the salts of copper and nickel have practically the same absorption spectra as the conducting solutions of salts of these metals, and the color of these solutions can not be attributed to the presence of copper and nickel ions.

Summary and Conclusions.

1. The copper, cobalt, nickel, ferric, manganese, chromium, and lead stearates and the copper, cobalt, and nickel palmitates have been prepared and described. Stannic stearate was prepared by double decomposition in benzene. A number of such instantaneous double decompositions with the stearates and palmitates in insulating solutions was noted. Such instantaneous precipitations can therefore not be attributed to the unsaturated condition of the acid radical as claimed by Cady.

2. The solubility of the above mentioned salts was determined in pyridine, benzene, toluene, carbon bisulfide, chloroform, carbon tetrachloride, amyl alcohol, methyl alcohol, ether, acetone, ethyl acetate, paraffin, and heptane.

3. A series of crystalline compounds of some of the stearates and palmitates with pyridine was obtained. A number of these compounds have been described and their formulae determined by analysis. These data would be valuable as a means of purifying the stearates and palmitates of the heavy metals. They were also of interest because they fit in a series of analogous crystalline addition products of the salts of other organic acids with nitrogen bases.

4. Cobalt stearate and palmitate, when dissolved in a number of solvents such as paraffin, phenol, naphthalene, and toluene, and even the dry salts themselves, were found to change from pink to blue when they were heated. This would indicate that the change in color which is well known in aqueous solutions of cobalt salts, can not be due to hydration or the presence of ions in the solution, but is probably due to some intramolecular change.

5. The absorption spectra of the aqueous solutions of the chlorides of copper, cobalt, and nickel and of the pyridine and carbon tetrachloride solutions of the stearates of these metals have been photographed. No fundamental difference has been noted in the absorption spectra of the aqueous and non-aqueous solutions.

The author wishes to take this opportunity of thanking Professor Kahlenberg for his valuable suggestions during the progress of this work which was undertaken at his request.

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THE PREPARATION OF COMPOUNDS OF TRYPAN-RED WITH IODINE AND OTHER SUBSTANCES.

BY ROBERT B KRAUSS.

Received January 24, 1914.

It was found by Lewis[1] in 1912 in this laboratory that certain dyes, namely, trypan-red, trypan-blue, and isamine-blue, had a more or less selective affinity for different portions of the tuberculous tissue experimentally produced in the rabbit. Trypan-red, for example, when injected into a living animal which was suffering from tuberculosis, would be found after several days in considerable concentration in the central, more or less necrotic portions of the diseased tissues.

It was thought possible that this fact might be used as the basis for an attempt to distribute various physiologically active substances to the diseased tissue. Iodine was the active substance first selected. It was chosen because it is one of the few substances having any sustained reputation among physicians as a useful agent in the treatment of certain forms of localized tuberculosis. It is my purpose to present here, as briefly as possible, the purely chemical aspects of the work so far done. The physiological results obtained with the use of the substances whose preparation and analyses are presented in this paper will shortly be reported in an appropriate place.

The chemical problem, accordingly, was to prepare compounds allied physiologically to trypan-red and containing iodine in the molecule. We have been able to obtain three direct substitution products of trypan-red with iodine. A compound of iodoform and trypan-red has been produced. We were able to obtain compounds of the dyestuff with thymol, eucalyptol, guaiacol, phenol, the cresols, cinnamic esters and pyrrol. The compounds with these substances have been further varied by substitution with iodine.

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[1] Paul A. Lewis, "The Selective Relation of Certain Vital Stains to the Tubercle," *Arch. Intern. Med.*, 10, 68 (1912).

Experimental.

Method of Analysis.—The elementary analyses mentioned in this paper were conducted according to Dennstedt's simplified method, with the modification that a platinum capillary insert was used in place of the glass capillary of the original method, in order to avoid loss of time from breakage of the latter. Also, glass tubing with rubber connections was substituted for the rubber tubing of the method where it was feasible to do so, the former combination being sufficiently flexible to serve the purpose, obviating thereby the constant absorption of moisture through the rubber into the system.

Determinations of iodine were carried out also by the method of E. C. Kendall,[1] with slight modifications. These were for the most part very kindly furnished by Kendall himself, in the form of additional notes to his paper. We have made one slight departure of our own. This consisted of heating the crucibles in a firebrick[2] furnace having an insert (Fig. 1). By this means they were heated more indirectly and evenly than possible in his method. At the same time contamination from gases was totally eliminated.

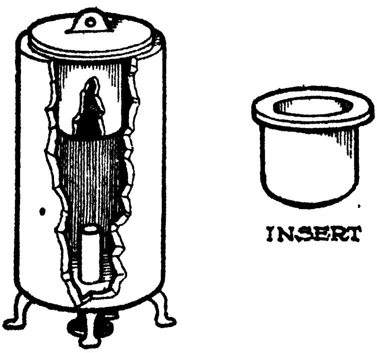
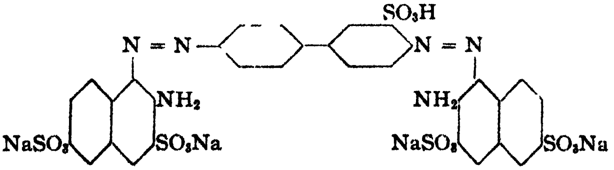


FIG. I

Trypan-red is a red dye very soluble in water, insoluble in alcohol. The manufacturers have not, to our knowledge, patented the preparation and have furnished no data as to its composition or the methods used in its manufacture. Ehrlich and Shiga first called attention to this dyestuff which they used in experiments, now classical, in the treatment of experimental infections with trypanosomes.

According to Ehrlich and Shiga[3] the composition of trypan-red is: Tetrazobenzidine monosulfonic acid (1 mol) coupled to β-naphthylamine disulfonate of sodium, R salt (2 mols). Structural formula:



These authors furnish no analyses of the substance and we are familiar with no published evidence for the formula given. Of the dyestuffs furnished commercially, even the purest does not correspond to this formula. In the various specimens analyzed wide variation in the sulfonic acid radical content was observed, as well as foreign organic substances, such as benzidine sulfone-sulfonic acid, benzidine di- and trisulfonic acids coupled variously with aminonaphthol sulfonic acids, Neville and Whinther's acid, amino G acid, amino R acid and amido H acid.

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[1] E. C. Kendall, This Journal, 34, 894 (1912).

[2] Crucible furnaces of this design made of fire clay in three pieces have been recently made to our order at a reasonable cost.

[3] Ehrlich and Shiga, *Berl. klin. Wochenschrift*, 41, 13 (1904).

In the purification of the trypan-red considerable difficulty was accordingly encountered. It was deemed advisable to avoid separations with saline solutions owing to the difficulty of completely removing inorganic salts from the purified dyestuff. The purification was accomplished by a rather tedious fractional precipitation, using alcoholic solutions of widely variable concentration in conjunction with acetic and hydrochloric acids. The analysis of the purified material gave values approximately called for by the formula ($C_{32}H_{20}N_6S_5Na_4O_{15}$) of Ehrlich. The following is an example:

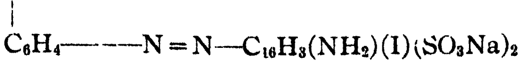
Calc. C, 39.18; H, 2.04; N, 8.57; S, 16.33; Na, 9.39

Found: C, 39.20, 39.24; H, 2.14, 2.10; N, 8.59, 8.63; S, 16.40, 16.52, Na, 9.30, 9.34

In the interpretation of such results as we have obtained, we have assumed the substantial correctness of the formula. We have made certain attempts to prepare trypan-red from our own materials. When we have worked with purified components we have never succeeded in making the dye. On the other hand, as the result of the combination of impure benzidine monosulfonic acid as a rough sulfonation product and an impure R salt we have obtained a mixture of substances, from which we have been able to separate a large proportion of a dye having the chemical and biological characteristics of trypan-red.

We mention this matter because of its bearing on our failure to get some results which might have been expected from the formula. Briefly, benzidine monosulfonic acid can be combined with iodine in at least five different proportions. We have never, however, been able to combine the iodized benzidine with pure R salt in such a way as to give any substance having a resemblance biologically to trypan-red. In view of our failure to prepare trypan-red from pure components we do not consider it certain that iodized trypan-red with iodine substituted benzidine cannot be prepared. As above stated, we have been able to make a number of preparations containing iodine in the molecule and more or less closely resembling trypan-red in their biological properties. The methods which we have used, the analyses of the preparations and their probable formulas are briefly presented in the following paragraphs:

Compound $C_{32}H_{19}O_{15}N_6S_5Na_4I$, *Monoiodo Trypan-red*



$$\begin{array}{l} C_6H_3(SO_3)-N=N-C_{10}H_4(NH_2)(SO_3Na)_2 \quad 2:3:6 \\ | \\ C_6H_4-\!\!-\!\!-N=N-C_{10}H_3(NH_2)(I)(SO_3Na)_2 \end{array}$$

Tetrazobenzidine monosulfonic acid coupled to monoiodo-β-naphthylamine disulfonic salt R and β-naphthylamine disulfonic R salt. This was prepared by treating 25 g. trypan-red in a flask with 16 g. of potassium iodide and 125 cc. water, then adding 25 cc. conc. sulfuric acid. The flask is attached to a reflux condenser and heated to boiling for an hour. After neutralizing with sodium carbonate solution the dyestuff is filtered, washed with dilute alcohol, absolute alcohol and dried at 110°. It is a crimson powder, soluble in water to a red solution. It is insoluble in alcohol, ether and benzol. Analysis:

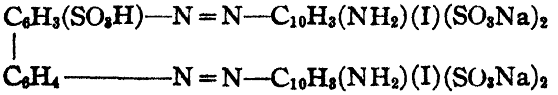
Calc. for $C_{32}H_{19}N_6S_5Na_4IO_{16}$: C, 34.72; H, 1.42; N, 7.59; S, 14.47; Na, 8.31; I, 11.48

Found: C, 34.76, 34.78; H, 1.70, 1 74; N, 7.58, 7 60; S, 14.48, 14.50; Na, 8.32, 8.34; I, 11.47, 11.47

When treated with KOH solution the dye turns to a violet color; with concentrated H_2SO_4, blue; on heating, iodine is given off.

Determination of the Location of the Iodine. The dyestuff was dissolved in a little water and the solution made strongly alkaline with ammonia; zinc dust was then added and the solution heated to boiling, whereupon the the color disappeared. On acidifying, cooling, and filtering, the benzidine monosulfonic acid remains with the zinc dust on the filter, while the second components are in the filtrate as *o*-diamino sulfonic salts. The benzidine monosulfonic acid, when dissolved from the zinc, evaporated to dryness, and treated with concentrated sulfuric acid and warmed, does not give off any iodine. The filtrate from the zinc containing the naphthylamine fraction of the dye shows distinctly this reaction, therefore: All the iodine present is located in the β-naphthylamine disulfonic salt, and since one atom of iodine is present, only one molecule of the second component has been substituted.

Compound $C_{32}H_{18}N_6S_5O_{16}Na_4I_2$, *Di-iodo Trypan-red*



$$\begin{array}{l} C_6H_3(SO_3H)—N=N—C_{10}H_3(NH_2)(I)(SO_3Na)_2 \\ | \\ C_6H_4————N=N—C_{10}H_3(NH_2)(I)(SO_3Na)_2 \end{array}$$

Tetrazobenzidine monosulfonic acid coupled to monoiodonaphthylamine disulfonic acid R and monoiodonaphthylamine disulfonic acid R. This was obtained by treating 25 g. of trypan-red in a flask with 100 cc. of 50% alcohol and 50 cc. of saturated alcoholic solution of iodine in the presence of mercuric oxide. The flask is boiled under reflux for three hours. After cooling, the dye is filtered off and washed on the filter with alcohol, dissolved from the filter in hot water, the solution made acid with hydrochloric acid, saturated with hydrogen sulfide to remove any mercury present, filtered, boiled to expel hydrogen sulfide, filtered and evaporated to dryness. A red dyestuff is obtained which dissolves in water to a deep red solution. Reduction and examination, as before, showed the iodine to be present only in the β-naphthylamine salt.

Calc. for $C_{32}H_{18}N_6S_4Na_4I_2O_{16}$ C, 31 20, H, 1 46, N, 6 82, S, 12 98, Na, 7 47, I, 20 61
Found C, 31 11, 31 00, H, 1 46, 1 48, N, 6 81, 6 76, S, 12 96, 12 88, Na, 7 48, 7 50, I, 20 59, 20 60

On treating the dye with concentrated potassium hydrate solution the color becomes violet, with concentrated sulfuric acid, blue, and on heating iodine is given off.

Iodoform Trypan red—On heating trypan red with a large excess of iodoform in alcoholic solution under reflux for six hours, a dark brown compound of iodoform and trypan red results The dye is washed with alcohol until no more iodoform can be detected in the washings and then dried at 130° This insures the removal of any remaining free iodoform

On standing, iodoform is slowly liberated only after considerable time Heating with conc H_2SO_4 turns the dye blue and iodoform is given off, with caustic potash the color change is to red violet The dried red brown dye is completely soluble in water to bright red solution

Calc for $C_{32}H_{20}N_6S_4Na_4O_{14}$ CHI_3 I 28 60 Found I 28 59 28 60, 28 61 28 54

Compound, $C_{32}H_{16}N_4O_{16}S_6Na_4I_4$, *Tetraiodo Trypan red* —By means of the Sandmeyer reaction, trypan red yields an iodine derivative of dark brown color, which dissolves in water to a deep red solution with a violet tinge Analysis showed the iodine to be present in the naphthalene disulfonic salt, and corresponding to four atoms iodine

Calc for $C_{32}H_{16}N_4S_6Na_4I_4O_{16}$ C 26 37 H, 1 09, S 10 98, N, 3 84 Na 6 31, I, 34 89
Found C 26 37 26 20, H, 1 07, 1 04, S 10 85, 10 78, N 3 79 3 80, Na, 6 18 6 22, I, 34 87, 34 79, 34 88

Formula $C_6H_3(SO_3H)-N=N-C_{10}H_2I_2(SO_3Na)$

$C_6H_4 - - - - N\ \ N- C_{10}H_2I_2(SO_3Na)$

Concentrated H_2SO_4 turns the dye dark blue and liberates iodine on warming, caustic potash gives a dark red color

Compound, $C_{32}H_{16}N_4O_{17}S_6Na_4I_4$, *Diiodo-diiodoso Trypan red* The preceding preparation dissolved in 20% sodium hydroxide was treated with a current of chlorine gas. The temperature of the solution was kept constant at 40° A diiodo-diiodoso trypan-red was formed, having an active oxygen content of 2 09% It oxidizes hydriodic acid, liberating iodine. This may be separated by shaking with chloroform and then can be titrated with thiosulfate

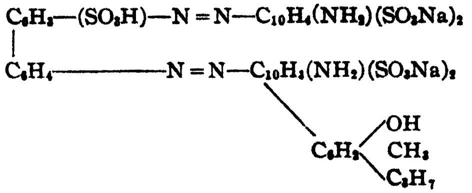
Calc. for $C_{32}H_{16}N_4S_6Na_4I_4O_{17}$ C 25 80, H, 1 08, N, 3 76 S 10 75 Na 6 04 I 34 14 Active O, 2 09
Found C, 25 81, 25 63, H 1 07 1 05, N 3 70, 3 78 S 10 70 10 65 Na 6 06 6 10, I, 34 08 33 91, Active O, 2 09 2 07

$C_6H_3-(SO_3H)-N=N-C_{10}H_3(I)(I=O)(SO_3Na)$

C_6H_4————————$N=N-C_{10}H_3(I)(I=O)(SO_3Na)_2$

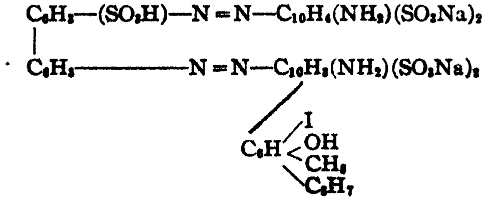
Compound, $C_{42}H_{32}N_6O_{16}S_6Na_4$, *Thymol Trypan-red*—This dyestuff is formed when 25 g. trypan-red, 300 cc. 50% alcohol and 15 g. thymol are boiled together in a flask under reflux for 24 hours. It is a crimson dye of the above composition, soluble in water to a crimson solution and insoluble in alcohol. The dye turns dark blue with concentrated sulfuric acid, liberating thymol on heating. With caustic potash the color is yellow-red.

Calc. for $C_{42}H_{32}N_6Na_4S_5O_{16}$: C, 44.68; H, 2.83; N, 7.44; Na, 8.15; S, 14.18.
Found: C, 44.72, 44.82; H, 2.88, 2.90; N, 7.48, 7.54; Na, 8.16, 8.25; S, 14.20, 14.28.


C₆H₃—(SO₃H)—N = N—C₁₀H₄(NH₂)(SO₃Na)₂
C₆H₄—N = N—C₁₀H₃(NH₂)(SO₃Na)₂
OH
C₆H₂
CH₃
C₃H₇

Compound, $C_{42}H_{31}O_{16}N_6S_5Na_4I$, *Iodothymol Trypan-red.*—Thymol trypan-red (25 g.) was treated with 30 g. sodium hydroxide, 200 cc. water, and 10 g. iodine and then warmed to 80°. As soon as the reaction is completed the solution is neutralized with hydrochloric acid, the dyestuff separating out. It is washed on the filter with alcohol and dried. The scarlet powder is soluble in water to a scarlet solution. On warming the dye with concentrated H_2SO_4 iodine is liberated.

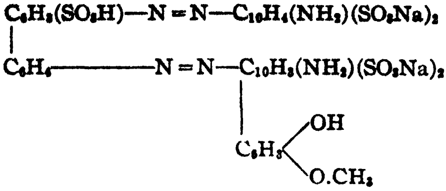
Calc. for $C_{42}H_{31}N_6Na_4S_5I.O_{16}$: C, 40.18; H, 2.47; N, 6.69; S, 12.75; Na, 7.34; I, 10.12.
Found: C, 40.18, 40.12; H, 2.50, 2.62; N, 6.65, 6.68; S, 12.80, 12.72; Na, 7.32, 7.19; I, 10.08, 10.16.


C₆H₃—(SO₃H)—N = N—C₁₀H₄(NH₂)(SO₃Na)₂
C₆H₃—N = N—C₁₀H₃(NH₂)(SO₃Na)₂
I
C₆H
OH
CH₃
C₃H₇

Compound, Eucalyptol Trypan-red.—This was formed when 15 g. trypan-red, 5 g. eucalyptol, and 50 cc. of 80% alcohol are heated under reflux to boiling for three hours. The insoluble eucalyptol trypan-red is filtered off and washed with alcohol. It is a red-brown dye of varied composition, soluble in water to a red solution. An iodine derivative of this dyestuff was also prepared.

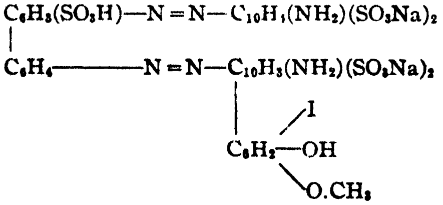
Compound, $C_{39}H_{28}N_6O_{17}S_5Na_4$, *Guaiacol Trypan-red.*—Finely divided trypan-red (25 g.) is heated with 10 g. guaiacol and 300 cc. 50% alcohol, for three hours under reflux. On cooling, the dyestuff settles out, is filtered, and washed with alcohol and dried at 110°. It is a red-brown powder soluble in water to a red solution with a yellow tinge.

Calc. for $C_{39}H_{28}N_6S_5Na_4O_{17}$: C, 42.39; H, 2.62; N, 7.60; S, 14.48; Na, 8.34.
Found: C, 42.39, 42.27; H, 2.61, 2.66; N, 7.61, 7.64; S, 14.49, 14.20; Na, 8.33, 8.41.



Compound, $C_{39}H_{25}N_6O_{17}S_5Na_4I$, *Iodoguaiacol Trypan-red.*—Prepared by heating 15 g. trypan-red, 6 g. iodoguaiacol and 150 cc. 50% alcohol as under the preceding. The dark brown dye which results is soluble in water to a red solution with a slight yellow tinge. Sulfuric acid liberates iodine from the dye on heating. Caustic potash gives a yellow-red color.

Calc. for $C_{39}H_{25}N_6S_5Na_4IO_{17}$: C, 38.08; H, 2.11; N, 6.84; S, 13.02; Na, 7.49; I, 10.34. Found: C, 38.17, 38.07; H, 2.12, 2.14; N, 6.82, 6.76; S, 13.01, 13.06; Na, 7.47, 7.50; I, 10.33, 10.28.



Compound, $C_{36}H_{23}N_7O_{15}S_5Na_4$, *Pyrrol Trypan-red.*—When 15 g. trypan-red, 5 g. pyrrol and 100 cc. of 50% alcohol are heated under reflux for three hours, a condensation of pyrrol and trypan-red takes place and a red-brown dye of the above composition is formed. It is soluble in water to a yellow-red solution and insoluble in alcohol and ether. The dye does not give a reaction for pyrrol with isatin and sulfuric acid or phenanthraquinone.

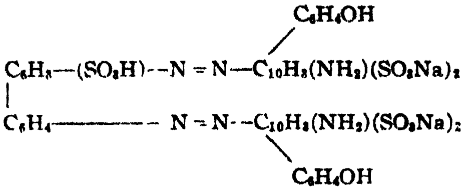
Calc. for $C_{36}H_{23}N_7Na_4S_5O_{15}$: C, 41.27; H, 2.39; N, 9.35; Na, 8.79; S, 15.28.
Found: C, 41.26, 41.20; H, 2.39, 2.35; N, 9.34, 9.38; Na, 8.78, 8.82; S, 15.30, 15.27.

Compound, $C_{36}H_{19}N_7O_{15}S_5Na_4I_4$, *Tetraiodopyrrol Trypan-red.*—This dye is formed when tetraiodopyrrol (from pyrrol and iodine in alkaline solution) is treated with trypan-red as in the preparation of pyrrol trypan-red. The tetraiodo dye is a dark brown salt soluble in water to a red solution. On addition of concentrated H_2SO_4 the dye turns blue and iodine is liberated on warming.

Calc. for $C_{36}H_{19}N_7I_4Na_4S_5O_{15}$: C, 27.88; H, 1.23; N, 6.32; I, 32.79; Na, 5.94; S, 10.32.
Found: C, 27.85, 27.80; H, 1.28, 1.35; N, 6.31, 6.28; I, 32.75, 32.70; Na, 5.96, 5.93; S, 10.31, 10.42.

Compound, $C_{44}H_{28}N_6O_{17}S_5Na_4$, *Phenol Trypan-red.*—Obtained by heating trypan-red under reflux with an excess of phenol in alcoholic solution for three hours. It is a crimson dye, soluble in water to a yellow-red solution. This dye does not give tests for phenol. On heating with concentrated sulfuric acid the phenol is split off.

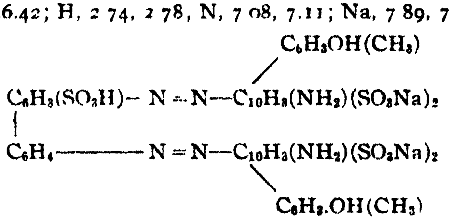
Calc. for $C_{44}H_{28}N_8Na_4S_5O_{17}$: C, 44.82; H, 2.37; N, 8.31; Na, 7.81; S, 13.58.
Found: C, 44.95, 44.90; H, 2.39, 2.57; N, 8.28, 8.26; Na, 7.68, 7.70; S, 13.51, 13.62.



$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad C_6H_4OH \\ \qquad\qquad\qquad\qquad\qquad\quad / \\ C_6H_3{-}(SO_3H){-}{-}N = N{-}C_{10}H_3(NH_2)(SO_3Na)_2 \\ | \\ C_6H_4{-}{-}{-}{-}{-}{-}{-}{-}N = N{-}{-}C_{10}H_3(NH_2)(SO_3Na)_2 \\ \qquad\qquad\qquad\qquad\qquad\quad \backslash \\ \qquad\qquad\qquad\qquad\qquad\qquad C_6H_4OH \end{array}$$

Compound, $C_{46}H_{32}N_6O_{17}S_5Na_4$, *Di-o-cresol Trypan-red.*—On heating trypan-red with an excess of alcoholic *o*-cresol under reflux for three hours, a red-brown dye is formed which is soluble in water to a red solution. The dye is not broken down by heating the solution, nor can a test for cresol be obtained. Boiling with conc. sulfuric acid turns the dye blue and splits off cresol.

Calc for $C_{46}H_{32}N_6Na_4S_5O_{17}$ C, 46.30, H, 2.68; N, 7.04; Na, 7.71; S, 13.42.
Found. C, 46.26, 46.42; H, 2.74, 2.78, N, 7.08, 7.11; Na, 7.89, 7.73; S, 13.38, 13.30



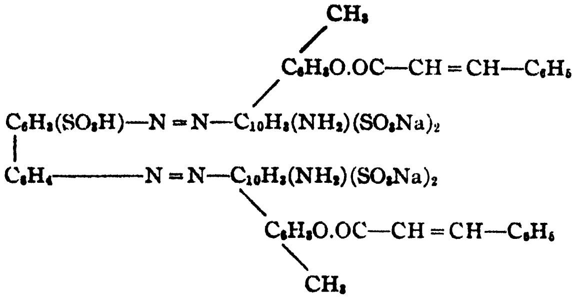
$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\quad C_6H_3OH(CH_3) \\ \qquad\qquad\qquad\qquad\qquad / \\ C_6H_3(SO_3H){-}\ N = N{-}C_{10}H_3(NH_2)(SO_3Na)_2 \\ | \\ C_6H_4{-}{-}{-}{-}{-}{-}{-}N = N{-}C_{10}H_3(NH_2)(SO_3Na)_2 \\ \qquad\qquad\qquad\qquad\qquad \backslash \\ \qquad\qquad\qquad\qquad\qquad\quad C_6H_3.OH(CH_3) \end{array}$$

In the same manner di-*m*-cresol trypan-red, a dark red-brown dye, and di-*p*-cresol trypan-red, a dark red-brown dye, were prepared. With sulfuric acid the *m*-derivative gives a violet-blue color and the *p*-derivative a dark blue color. By treating these three isomers with iodine in caustic soda solution, and then neutralizing with acid, their iodine substitution products are obtained. In this way were made di-*o*-triiodocresol trypan-red, $C_{46}H_{26}N_6O_{17}S_5Na_4I_6$; di-*m*-triiodocresol trypan-red, $C_{46}H_{26}N_6O_{17}S_5Na_4I_6$; di-*p*-triiodo cresol trypan-red, $C_{46}H_{26}N_6O_{17}S_5Na_4I_6$.

Calc. for 6I, 39.69%.
Found for *o*-deriv. 39.64, 39.64; *m*-deriv., 39.62, 39.65; *p*-deriv. 39.67, 39.70.

Compound, $C_{64}H_{44}N_6O_{19}Na_4S_5$, *Dicinnamyl-di-o-cresol Trypan-red.*—Prepared by treating, in a flask, 146 pts. di-*o*-cresol trypan-red, 18 pts. sodium cinnamate, and 100 pts. benzene in the cold with 9 pts. phosporous pentachloride and then heated under reflux until the evolution of hydrochloric acid has ceased. The benzene is then poured off and the residue neutralized with sodium carbonate. It is a red dye soluble in water to a red solution. Sulfuric acid turns it blue and caustic soda to a yellow-red solution.

Calc. for $C_{64}H_{44}N_6Na_4S_5O_{19}$: C, 52.89; H, 3.03; N, 5.76; Na, 6.33, S, 11.01.
Found: C, 55.71, 52.76; H, 3.06, 3.14; N, 5.78, 5.81; Na, 6.31, 6.39; S, 10.97, 11.08.

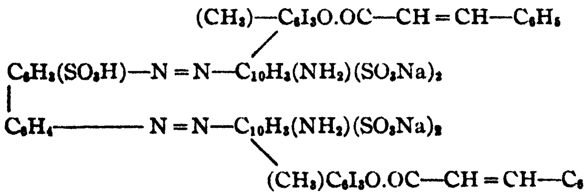

CH₃
C₆H₃O.OC—CH = CH—C₆H₅
C₆H₃(SO₃H)—N = N—C₁₀H₃(NH₂)(SO₃Na)₂
C₆H₄————N = N—C₁₀H₃(NH₂)(SO₃Na)₂
C₆H₃O.OC—CH = CH—C₆H₅
CH₃

Dicinnamyl-di-*m*-cresol Trypan-red. Color scarlet.

Dicinnamyl-di-*p*-cresol Trypan-red. Color dark red.

Compound, $C_{64}H_{38}O_{19}N_6S_5Na_4I_6$, *Dicinnamyl-di-o-triiodocresol Trypan-red.*— Prepared according to the method indicated in the preceding paragraph, using di-*o*-triiodo trypan-red as a starting point. The dyestuff obtained is a crimson powder easily soluble in water to a red solution, giving with concentrated sulfuric acid a blue color, and on heating this iodine is split off.

Calculated for $C_{64}H_{38}N_6Na_4S_5I_6O_{19}$: C, 34.78; H, 1.72; N, 3 80; Na, 4.16; S, 7.24; I, 34.51. Found: C, 34.76, 34 70; H, 1.68, 1.94; N, 3 79, 3.65; Na, 4 11, 4.23; S, 7.23, 7.21; I. 34.47, 34.43.


(CH₃)—C₆I₃O.OC—CH = CH—C₆H₅
C₆H₃(SO₃H)—N = N—C₁₀H₃(NH₂)(SO₃Na)₂
C₆H₄————N = N—C₁₀H₃(NH₂)(SO₃Na)₂
(CH₃)C₆I₃O.OC—CH = CH—C₆H₅

Dicinnamyl-di-*m*-triiodocresol Trypan-red. A crimson powder.

Dicinnamyl-di-*p*-triiodocresol Trypan-red. A red powder.

Concentrated sulfuric acid turns both of these dyes dark blue and iodine is then split off on heating.

The cinnamyl esters of the remaining phenolic condensations mentioned are being prepared in this laboratory.

Summary.

1. Iodine derivatives of trypan-red of similar color, solubility and biological qualities were prepared.
2. An iodoform addition product of trypan-red of definite composition was prepared.
3. Condensation products of trypan-red and phenol, the cresols, thymol, guaiacol, pyrrol and their iodine substitution products of definite compositions were prepared.
4. Condensation products of trypan-red with eucalyptol and its iodine derivative of indefinite composition were prepared.

5. Cinnamic esters of the cresol trypan-reds and of the iodocresol trypan reds of definite composition were prepared.

In conclusion the author wishes to express his gratitude to Paul A. Lewis, who suggested the present investigation.

PHILADELPHIA, PA

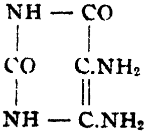
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON PYRIMIDINES. LXIX. ON A COLOR TEST FOR 5-AMINOPYRIMIDINES.

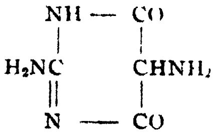
BY TREAT B. JOHNSON AND CARL O. JOHNS.

Received February 25, 1914.

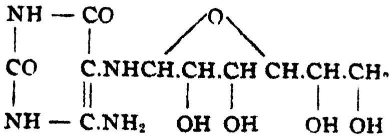
In the last paper from this laboratory on pyrimidines entitled, "The Structure of Ritthausen's Divicine,"[1] the writers emphasized the significance of the interesting observation made by Ritthausen,[2] that this base interacts with phosphomolybdic acid, in aqueous solution, giving an intense blue color. We contributed the interesting data that 4,5-diaminouracil (I) and 2,5-diamino-4,6-dioxypyrimidine (II) likewise interact with this reagent, giving apparently the same blue color as *divicine*. Phosphotungstic acid also gave a characteristic blue color with the 2,5-diamino-4,6-dioxypyrimidine (II), but, on the other hand, the isomeric 4,5-diaminouracil interacted with formation of an amorphous green precipitate. This behavior is in accordance with that of divicine towards phosphotungstic acid. In fact, all the known experimental evidence seems to indicate that Ritthausen was actually dealing with this pyrimidine and, consequently, that his *vicine*, which he isolated from vetch seeds, is a glucoside of this interesting base as represented by formula (III).[3] Whether these assumptions are correct will be determined by an examination of the natural products. This work is now in progress.



(I)



(II)



(III)

Attention was also called, in our paper, to the fact that both of the diaminopyrimidines contain an amino group in position 5 of the pyrimidine ring, and we stated therein that we should present, in a later paper, new evidence in support of the assumption that it is probably this particular amino group which actually participates in this characteristic color reaction. This work has been continued, and the new data, which we have already obtained, are now recorded in this paper.

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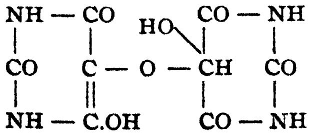
[1] Johnson and Johns, THIS JOURNAL, 36, 545 (1914).

[2] *J. prakt. Chem.*, 59, 482.

[3] The sugar might also be linked to the 4-amino group of the pyrimidine base.

Folin and Dennis[1] have recommended as an uric acid reagent a phosphotungstic acid solution, which is prepared by treatment of sodium tungstate in aqueous solution with a definite amount of phosphoric acid. They found that this reagent not only interacts with uric acid in the presence of sodium carbonate, with formation of a blue color, but also gives characteristic blue solutions with monohydric phenols containing an amino group in the benzene ring, and also with di- and polyhydric phenols. As a specific phenol reagent, these investigators recommend a phosphotungstic acid solution which contains 10% of sodium tungstate, 2% of phosphomolybdic acid and 10% of phosphoric acid. This mixture not only gives a blue color with uric acid, but also with all phenols which Folin and Dennis examined, with the exception of *o*-, *m*- and *p*-nitrophenols.[2] In fact, they state that the solution can be used as a substitute for Millon's reagent. Both reagents are applied by mixing them with an aqueous solution of the compound to be tested, and then adding the required amount of alkali to produce the color. Folin and Dennis state that the color is produced in alkaline solutions only, and is not obtained if the alkali is added before the phosphotungstic acid reagent. They recommend sodium carbonate as the alkali to be used and expressly state that potassium carbonate and ammonium hydroxide can not be used, because they give precipitates with the reagents.

These solutions of Folin and Dennis were later used by Funk and Macallum[3] in an investigation of the chemical nature of substances from alcoholic extracts of various foodstuffs. They found, for example, that this solvent dissolved nitrogenous substances, which reacted, in many cases, with the uric acid and phenol reagents giving blue colors. In order to acquire a knowledge of the nature of compounds capable of reacting in this characteristic manner they examined the behavior of the two reagents towards various substances of biochemical interest. Several pyrimidine and purine compounds were included among those tested. Alloxantine (IV), however,



(IV)

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[1] *J. Biol. Chem.*, 12, 239 (1912).

[2] The behavior of this reagent towards new types of phenols will be discussed in a future paper (T. B. J.).

[3] *Biochem. J.*, 7, 356 (1913).

was the only pyrimidine compound, of those examined, which interacted with formation of a blue color. Thymine, uracil, uridine and cytidine gave no color. The purines xanthine, hypoxanthine, guanine, 3-methyl- and 7-methyluric acids gave blue solutions with the phenol reagent while no color was obtained with the uric acid reagent. Adenine, paraxanthine, theophylline, guanosine and adenosine failed to react with either reagent.

This work of Funk and Macallum's was recently extended by an investigation of Lewis and Nicolet,[1] who examined the behavior of the two reagents towards about seventy different organic substances. These included a variety of hydantoin, pyrimidine and purine compounds. No generalizations, however, can be established from their data. The most striking results obtained by them were the observations, that certain hydantoins react positively, and that the only two sulfur-free pyrimidines, which interacted with formation of a blue color, were 2,4,5-triamino-6-oxypyrimidine and 2,5-diamino-4,6-dioxypyrimidine (II). Of the twelve sulfur-free purines examined not one reacted positively.

Our investigation has so far been confined exclusively to the study of pyrimidine compounds. We have used both the uric acid and the phenol reagents of Folin and Denis, and also a third reagent or 2% phosphomolybdic acid solution. We have not applied the tests, however, as previously recommended and consequently have obtained some interesting and unexpected results. In fact, a systematic application of the three reagents has revealed some very interesting structural relationships. These are apparent by inspection of Table I.

Every compound represented in the table has been tested under the same conditions, *viz.*: in neutral,[2] acid and alkaline solutions. We have used acetic acid and ammonium hydroxide as the acid and alkali reagents, respectively. Twenty-nine different pyrimidines have been tested and also three related acyclic compounds, namely, cyanacetylurea, $NH_2.CO.NH.CO.CH_2.CN$, benzoylaminothioureaacrylic acid, $H_2NCSNHCOCH(NHCOC_6H_5)COOH$ and benzoylaminopseudo-ethylthioureaacrylic acid, $C_2H_5SC(NH_2) = NCH(NHCOC_6H_5)COOH$.

Methods Employed for the Application of the Tests.—Five to ten milligrams of the pyrimidine to be tested are dissolved in about 2–3 cc. of water, heat being applied if necessary. For a neutral test this solution was then cooled to the temperature of ordinary tap water and the respective reagent added directly. In applying the tests in acetic acid solution, the aqueous solution of the pyrimidine was first acidified with the reagent and the pyrimidine reagent then added. For testing in alkaline solution ammonium hydroxide was always used. The aqueous solution of the pyrimidine was made distinctly alkaline with this base and the pyrimidine reagent

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[1] *J. Biol. Chem.*, 16, 369 (1913).

[2] By neutral is meant without use of either acetic acid or ammonia.

TABLE I.

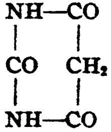
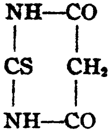
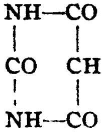
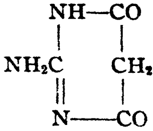
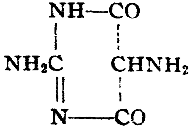
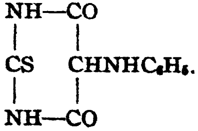
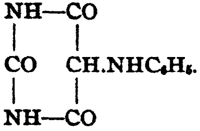
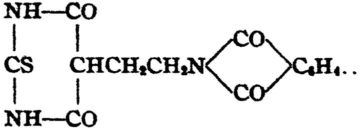
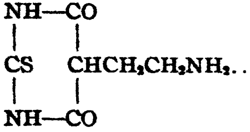
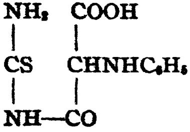
	Pyrimidines.	Phosphotungstic and phosphomolybdic acids. (Phenol reagent.)	Phosphomolybdic acid. (2% solution.)	Phosphotungstic acid. (Uric acid reagent.)	Solution.
1.	 (barbituric acid)	—	—	—	Acid (1)
		—	—	—	Alkaline (2)
		—	—	—	Neutral (3)
2.		—	—	—	1
		+ +	+ +	—	2
		—	—	—	3
3.	 (uramil)	—	—	—	1
		+ + + +	+ + + +	+ + + +	2
		—	—	—	3
4.		—	—	—	1
		+ +	+ +	—	2
		—	—	—	3
5.		+ + + +	+ + + +	—	1
		+ + + +	+ + + +	+ + + +	2
		+ + + +	+ + + +	—	3

TABLE I (*Continued*).

	Pyrimidines.	Phosphotungstic and phosphomolybdic acids. (Phenol reagent.)	Phosphomolybdic acid. (2% solution.)	Phosphotungstic acid. (Uric acid reagent.)	Solution.
6.		++++	+++	—	1
		++++	—	++++	2
		++++	+++	—	3
7.		green	green	—	1
		++++	—	++++	2
		++++	++++	+++	3
8.		—	—	—	1
		++	—	—	2
		—	—	—	3
9.		—	—	—	1
		++	—	—	2
		—	—	—	3
10.		++++	++++	—	1
		++++	++	++++	2
		++++	++++	+++	3

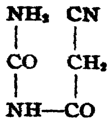
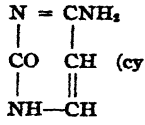
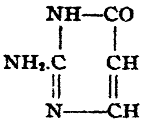
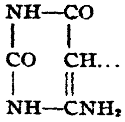
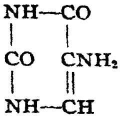
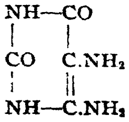
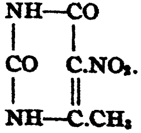
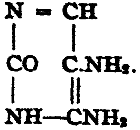
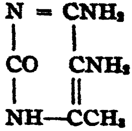
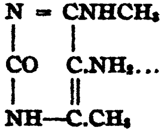
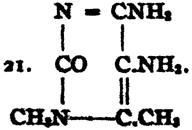
	—	—	—	1
11. 	+ + + +	+	—	2
	—	—	—	3
	—	—	—	1
12.  (cytosine)	—	—	—	2
	—	—	—	3
	—	—	—	1
13.  (isocytosine)	+ +	—	—	2
	—	—	—	3
	—	—	—	1
14. 	—	—	—	2
	—	—	—	3
	—	—	—	1
15. 	+ + + +	+ + + +	+ + + +	2
	—	—	—	3
	+ + + +	+ + + +	—	1
16.  (divicine?)	+ + + +	+	+ + + +	2
	+ + + +	+ + + +	—	3

TABLE I (*Continued*).

Pyrimidines.	Phosphotungstic and phosphomolybdic acids. (Phenol reagent.)	Phosphomolybdic acid. (2% solution.)	Phosphotungstic acid. (Uric acid reagent.)	Solution.
17. 	—	—	—	1
	—	—	—	2
	—	—	—	3
18. 	—	—	—	1
	+ + + +	+ + + +	+ + + +	2
	—	—	—	3
19. 	—	—	—	1
	+ + + +	+ + + +	+ + + +	2
	—	—	—	3
20. 	—	—	—	1
	+ + + +	+ + + +	+ + + +	2
	—	—	—	3
21. 	—	—	—	1
	+ + + +	+ + + +	+ + + +	2
	—	—	—	3

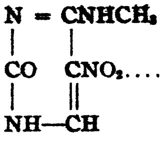
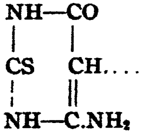
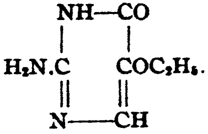
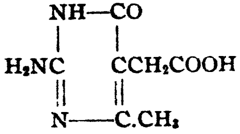
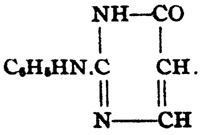
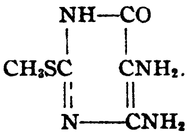
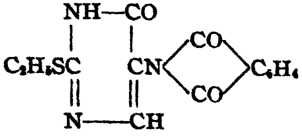
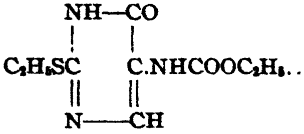
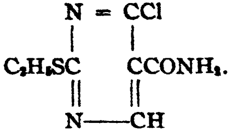
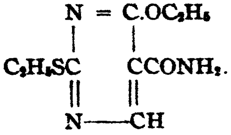
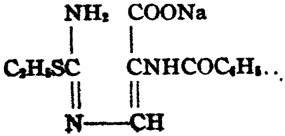
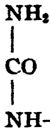
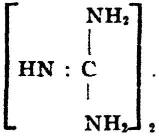
22.		—	—	—	1
		—	—	—	2
		—	—	—	3
23.		—	—	—	1
		—	—	—	2
		—	—	—	3
24.		—	—	—	1
		+ +	+ +	—	2
		—	—	—	3
25.		—	—	—	1
		+ +	+ +	—	2
		—	—	—	3
26.		—	—	—	1
		+ +	+ +	—	2
		—	—	—	3
27.		+ + + +	+ (strong)	—	1
		deep green	deep green	+ (strong)	2
		+ + + +	+ + + +	—	3

TABLE I (*Concluded*).

Pyrimidines.	Phosphotungstic and phosphomolybdic acids. (Phenol reagent.)	Phosphomolybdic acid. (2% solution.)	Phosphotungstic acid. (Uric acid reagent.)	Solution.
28. 	—	—	—	1
	+ +	+ +	—	2
	—	—	—	3
29. 	—	—	—	1
	+ + +	+ + +	+ +	2
	—	—	—	3
30. 	—	—	—	1
	—	+ +	—	2
	—	—	—	3
31. 	—	—	—	1
	—	+ +	—	2
	—	—	—	3
32. 	—	—	—	1
	+ +	+ +	—	2
	—	—	—	3

33.	 $H_2N-CO-NH-CONH_2$ (biuret)...........................	—	—	—	1
		—	—	—	2
		—	—	—	3
34.	 $[HN:C(NH_2)_2]_2.H_2CO_3$ (guanidine carbonate).......	—	—	—	1
		—	—	—	2
		—	—	—	3

Explanations for Table I.

Intense or deep blue color = + + + +
Light blue color = + + + .
Very pale blue = + +
Greenish blue = + .
No formation of a blue color = —.

Literature References for Table I.

(1, 2, 4) Michael, *J. pr. Ch.*, [2] **35,** 456; *Am. Chem. J.*, **9,** 221. (15, 17) Behrend, *Ann.*, **240,** 3; Behrend and Grünwald, *Ann.*, **309,** 256. (5, 16, 23, 14) Traube, *Ber.*, **26,** 2536; **33,** 1382; *Ann*, **331,** 71. (12, 13, 18, 25, 26, 27, 28, 29, 32) Johnson, *Am. Chem. J.*, **34,** 199; Wheeler and Johnson, *Am. Chem. J*, **29,** 498; **29,** 501, Johnson and Clapp, *Ibid.*, **32,** 142; Johnson, Johns and Heyl, *Ibid.*, **36,** 166; Johnson and Heyl, *Ibid.*, **38,** 668; Johnson and Johns, *J Biol. Chem*, **1,** 314; Johnson and Shepard, THIS JOURNAL, **35,** 1003. (30, 31) Wheeler and Johns, *Am. Chem. J.*, **38,** 597; **40,** 241 (19, 20, 21, 22, 24) Johns, *Am. Chem J*, **41,** 61; *J. Biol. Chem.*, **1,** 449; **11,** 397; **9,** 164; **16,** 140. (11, 33, 34) Kahlbaum's samples added last. Where a blue color was formed it generally developed immediately, before the formation of any precipitate. The colors produced in some cases were extremely intense and very permanent. As stated above 4,5-diaminouracil gives no color with the uric acid reagent in acid solution. When the test is applied according to the above conditions, in the presence of ammonia, an intense blue color is produced.

An examination of Table I will reveal the interesting fact that the 5-amino group is apparently the functionating group when phosphotungstic acid (uric acid reagent) produces a blue color in an ammoniacal solution. In every case examined by us the presence of an amino or imino group in the 5-position of the ring was necessary in order to obtain a blue color by use of the uric acid reagent. If both hydrogens were replaced by other groups or the 5-amino group placed in any other position in the ring or substituted in some side chain this reagent always failed to give a color in alkaline solution. It is interesting to note at this time that alloxantine also gives a blue color with the uric acid reagent in an ammoniacal solution. Whether other 5-hydroxypyrimidines behave in a similar manner will be determined by further work. 5-Hydroxypyrimidines possess many properties in common with the aromatic phenols.

NEW HAVEN, CONN.

NEW PROCESSES FOR THE PREPARATION OF BUTADIENE-1,3 HYDROCARBONS. II. PYROGENETIC DECOMPOSITION OF HYDROXY-COMPOUNDS.

BY L. P. KYRIAKIDES.

Received March 4, 1914

Part I. Catalytic Dehydration of Glycols.

In the first paper on these processes, it was shown that methyl 2-butylene-oxide-1,2 could be easily and smoothly dehydrated to isoprene. As oxides are anhydrides of the glycols, it occurred to me that the latter substances also might be made to give hydrocarbons of the butadiene-1,3 series. In the literature on the subject of dihydroxyl compounds, we read that α-glycols are easily transformed to aldehydes or ketones, after partial dehydration. This transformation is effected most readily by heating the glycols with dehydrating agents or dilute acids. The reactions[1] are explained on the assumption that the dehydration of the glycols results in the formation of either the corresponding oxide, or the homologue of vinyl alcohol. It is known that oxides are metamerized to aldehydes or ketones by the action of acid substances or high temperatures; while alcohols of the *vinyl* series, being incapable of existence in the free state, are metamerized to the carbonyl substances at the moment of their formation. Among the α-glycols, those containing two tertiary hydroxyl groups, the pinacones, are especially susceptible to such reactions. Pinacones are easily made to lose one molecule of water and then to give rise to ketones. This takes place by a molecular rearrangement, due to the wandering of an alkyl group. In the case of these ditertiary α-glycols, it has been observed that they can be made to lose two molecules of water and give rise to hydrocarbons with conjugated double bonds. This dehydration[1] is best carried out by distilling pinacone over alumina at 400°.

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[1] Lehrbuch der org. Chemie, Meyer-Jacobson, 2nd ed., Vol. I, Part I, pp. 648–649.

β-Glycols were studied by Lieben and his co-workers. If butandiol-1,3[2] is heated with dilute sulfuric acid, it is decomposed to a number of substances, among which *n*-butyraldehyde and methylethylketone are easily detected. That β-glycols, also, are mainly decomposed to substances containing the carbonyl group is further proven by the observations of Kadiera,[3] who obtained only butyraldehyde and methylethylketone by treating butandiol-1,3 with 50% sulfuric acid in the cold. Lieben[4] observes that the nature of the products obtained by the action of dehydrating agents, dilute acids or of water at high temperatures on β-glycols, depends on the constitution of the glycol. The main products are, then, aldehydes, ketones or 1,4-oxides. I began the study of the catalytic dehydration of the dihydroxyl compounds with the 1,3-glycols, which are, as a rule, more readily obtained than the α-isomers.

Butadiene-1,3 (Divinyl), $CH_2 : CH.CH : CH_2$.- *Divinyl* is the simplest representative of the hydrocarbons containing conjugated double bonds, and is capable of polymerization to a rubber-like mass. Harries,[5] who studied the hydrocarbon and its polymerization products, observes that the sodium butadiene rubber was vulcanized to a product that surpassed the other synthetic rubber-like substances in elasticity and strength. The handling of divinyl, which is a gas at ordinary temperatures, is not very easy. Our experience with this hydrocarbon was not very enjoyable, as in the majority of cases the sealed tubes exploded during the heating. The glycol used in the following experiments was obtained by the reduction of acetaldol.

Experiment I.[6]—95 g. β-butylene glycol were slowly dropped into a tube filled with pieces of ignited kaolin. The dehydration was effected at 380–400°, and the decomposition products were collected in a receiver cooled with a mixture of carbon dioxide and ether. The gaseous decomposition products were dried by passing them through a drying tower containing calcium chloride, and then condensed in a sealing tube. The amount of liquid condensed measured about 8 cc. This was treated with a little catalyst favoring normal polymerization, and submitted to the action of heat after sealing the tube. The latter was left in a steam bath for 72 hours, when the liquid was found to have thickened appreciably. In order to increase the rate of polymerization, the tube was heated in a bomb furnace at 120° for 72 hours more, and the hydrocarbon was thus made to solidify. On opening the tube we observed quite a little pressure, which was due to unpolymerized divinyl or other gaseous impurities. The solid product was submitted to steam distillation and was found to be a tough and elastic sample of a rubber-like substance. This substance, on being left in the air for a short time, is soon changed in its physical properties, becoming very hard and brittle. This is evidently the result of chemical changes due to oxidation.

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[1] D. R. P. 235,311, *Chem. Zentr.*, 1911, II, 112; Fr. Pat 417,275, *C A.*, 6, 2548 (1912).

[2] Bauer, *Monatsh.*, **25**, 1 (1904).

[3] *Monatsh.*, **25**, 340.

[4] *Ibid.*, **23**, 74 (1902).

[5] *Ann.*, **383**, 206, 213; **395**, 241, 259.

[6] This experiment was carried out on the 14th day of Dec., 1911.

Senderens,[1] in a review on the dehydration of saturated alcohols, remarks that the temperature and rate of catalysis are functions of the physical as well as chemical nature of the catalyst. Having studied the activity of a good many catalysts, Senderens concludes that carefully prepared and ignited aluminum oxide is the best catalyst; but the disadvantage in its use is that this substance is very sensitive towards impurities and heat. Kaolin and aluminum silicate are spoken of as being very active. Impurities and heat do not effect an appreciable decrease in the activity of these substances.

As we had on hand a sample of commercial aluminum phosphate, which was marked as *chemically pure*, we made use of it in the following experiment. Senderens speaks of aluminum phosphate as being only a fair dehydrating agent.

Experiment II.—75 g. of the glycol were catalyzed over ignited aluminum phosphate at 450° and 150 mm. The distillation of the liquid was carried out slowly, and the gases were condensed as in the last experiment. The water formed as a result of the reaction measured 28 cc.- -the theoretical amount is 30 cc. The organic layer had a very clean appearance, was very light yellow in color and measured about 50 cc. The gaseous products were partially purified by passing them through two bulbs containing concentrated potassium hydroxide, and then dried by means of calcium chloride. The alkaline liquids, contained in the bulbs, gradually deepened in color as the distillation of the gases progressed, and finally were covered with a little layer of a resinous substance. As the distillation of the dehydration products was finished by warming the receiver with the hand, any acetaldehyde present would be carried over into the alkaline solution, where it would be resinified. The production of acetaldehyde is probably due to the decomposition of any unreduced acetaldol present in the glycol. The divinyl as purified above was condensed in three tubes. The first tube, containing about 5 g. of the hydrocarbon and a few pieces of sodium, was sealed and heated at 60° for about 30 hours. The liquid was found to have solidified completely at the end of this period of heating. The contents of the tube were treated according to the directions of Harries, and the rubber was found to be fairly tough. The other two tubes, containing the hydrocarbon and a little of a catalyst, were sealed and heated one week at 100° and another at 110°. The liquid in one of the tubes was solid. The other tube, with the hydrocarbon still showing signs of mobility was heated for 15 hours more at 120°. The crude polymerization products were subjected to steam distillation and then dried. The substance obtained thus had the physical properties of crude rubber. It is seen that butadiene is more readily polymerized to a rubber-like substance than isoprene. In cases where the sample of divinyl was very impure, we could usually obtain a solid mass, no matter how small, on heating it for a week or two at 100 110°.

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[1] *Ann. chim. phys.*, [8] 25, 449 (1912).

The fact that the gases obtained by the pyrogenetic dehydration of butandiol-1,3 were capable of polymerization to rubber is ample proof of the formation of divinyl. In some catalyses the products of decomposition, especially those obtained in partial vacua (below 50 mm.) and at temperatures varying between 420 460°, were very clean in appearance and contained very little high boiling side-products. The low boiling products would easily solidify to rubber-like masses. A sample of such a decomposition product of β-butylene glycol was submitted to normal polymerization by heating in the steam bath. The liquid showed signs of rubber formation within 24 hours. The tube having exploded on the third day, we were able to recover about 5 g. of the divinyl as a very fair sample of rubber. The dehydration of the glycol had been effected by aluminum phosphate. Further evidence of the formation of considerable quantities of divinyl, even at ordinary pressures from β-butylene glycol, is found in the fact that on treating the decomposition products with bromine we were able to obtain great quantities of tetrabrombutane. This tetrabromide was dehalogenated according to Gustavson and Demjanoff's[1] zinc dust method, and the hydrocarbon polymerized to rubber. The choice of a good and active dehydrating agent in these catalyses is very essential. The dehydration of 1,3-glycols to hydrocarbons of the divinyl series, would seem to proceed according to the following course:

(1) $CH_3.CH(OH).CH_2.CH_2OH = CH_3.CH : CH.CH_2OH + H_2O.$

(2) $CH_3.CH : CH.CH_2OH = CH_2 : CH.CH : CH_2 + H_2O.$

R. B. Earle has been able to isolate crotonyl alcohol, $CH_3CH : CHCH_2$-OH, among the decomposition products in the formation of divinyl. In fact, β-butylene glycol, if submitted to the action of catalysts at temperatures not exceeding 350°, seems to be dehydrated principally to butenol. The assumption that crotonyl alcohol is an intermediate step in the complete dehydration of the glycol is supported by the discovery that buten-2-*ol*-1 itself, is readily dehydrated to butadiene-1,3, if subjected to the pyrogenetic action of catalysts. Charon,[1] furthermore, states that, by heating the bromo-ester of the unsaturated alcohol with potassium formate at 160–180°, he obtained the *diene* as the principal product of the reaction. The dehalogenation of bromo-1-butene-2 to divinyl is explained by Charon on the assumption that methylallene, $CH_3.CH : C : CH_2$, is the primary reduction product. This substance, however, is immediately isomerized to the more symmetrically constituted divinyl under the influence of the high temperature, the symmetrical configurations being the stablest of all.

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[1] *Chem. Zentr.*, **1888**, 1345; also Thiele, *Ann*., **308**, 339.

Isoprene, $CH_2 : C(CH_3).CH : CH_2$.—Methyl-2-butandiol-1,3, $CH_3.CH(OH).CH(CH_3).CH_2OH$, was obtained by the reduction of methyl-2-butanon-3-*ol*-1. Forty g. of the glycol were distilled slowly over aluminum phosphate at 450° and 15–20 mm. The decomposition products were condensed by means of carbon dioxide and ether. The products were separated from the water, dried and fractioned through a column. Ten g. of the liquid boiled at 30–40°. This was refractioned and 5 g. of the substance were obtained by boiling at 34–38°. The low yield of isoprene is explained on the assumption that the rate of catalysis was rather fast. The remarks as to the purity of the hydrocarbon, found in the last paper, would hold true here also. For a very pure sample of isoprene a higher vacuum, than the one used here, must be utilized.

Piperylene, $CH_3.CH : CH.CH : CH_2$.—The pentandiol, 2,4-$CH_3.CH(OH).CH_2.CH(OH).CH_3$, was prepared by the reduction of hydracetylacetone, $CH_3CH(OH)CH_2COCH_3$. Forty grams of the glycol were dehydrated at about 35 mm. as the isoprene above. The water formed as the result of the decomposition amounted to 12 cc.; theory calls for 14 cc. The dried organic liquid was fractioned through a column. A little liquid distilled over below 35°, and had the sharp smell of ethanal, which was probably due to the decomposition of unreduced hydracetylacetone present in the glycol. The fraction collected as piperylene boiled mostly at 40–45° and weighed more than 10 g.

I would like to mention here a reaction, which I did not have the time to study well, but which may, nevertheless, prove to be of considerable importance. It has been known for some time that finely divided copper,[2] made by the reduction of the oxide, has a catalytic action on alcohols at about 300°. Primary and secondary alcohols are thus dehydrogenated to aldehydes and ketones respectively; while tertiary alcohols[3] are dehydrated to olefines. On the basis of this last reaction, it seemed to me that a ditertiary α-glycol, such as pinacone, might be dehydrated so as to give rise to a homologue of divinyl. At 300° freshly reduced copper does not catalyze pinacone to a hydrocarbon. The pinacone used was obtained by distilling pinacone hydrate through a column until the temperature of the vapors attained 115°, and the residue from this distillation was made use of in the following experiments.

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[1] *Ann. chim. phys.*, [7] 17, 234.

[2] Sabatier and Senderens, *Bull. soc. chim.*, [3] 33, XVII, 263 (1905),

[3] *Ibid.*, also Neave, *The Analyst*, 34, 346 (1909).

Dimethyl-2,3-butadiene-1,3, $CH_2 : C(CH_3).C(CH_3) : CH_2$. — Thirty grams of the glycol were slowly distilled over finely divided copper at 430°. The distillate was freed from the water, dried over calcium chloride and fractioned through a column. Five grams of the liquid distilled over below 85°, mostly 70 75°. This liquid had the boiling point of dimethyl-2,3-butadiene-1,3 and the characteristics of an unsaturated hydrocarbon. The substance was dissolved in ether, cooled and treated slowly with bromine. The halogen was absorbed instantly. The addition of bromine was discontinued when the rate of its absorption slowed down appreciably. The solvent was then evaporated off, and the residue left in the ice-chest. We soon observed the deposition of a crystalline substance, which was very probably the tetrabromide of the hydrocarbon. The high boiling fraction from the distillation of the hydrocarbon contained pinacoline. Pinacoline itself, passed over freshly reduced copper at 450–480°, does not undergo any appreciable change. Another experiment was carried out with 40 g. pinacone. The temperature of reaction was kept at 460–500° and the pressure was that obtained by the May-Nelson vacuum pump. The decomposition products were collected at ordinary pressures at the exit end of the pump. The distillate was dried and fractioned through a Young's column, when 5 g. of the liquid distilled over below 90°. This substance was refractioned, and the liquid, boiling at 70° and amounting to 3 g., was brominated as above. In this case also, some of the crystalline tetrabromide was obtained. It seems evident that ditertiary α-glycols can be dehydrated to hydrocarbons of the butadiene-1,3 series, if they are distilled over freshly reduced copper at temperatures above 400°. The dehydration of these glycols could result, normally, only in the formation of pinacolines or hydrocarbons, which can be easily separated by fractional distillation. In the case of pinacone it may be possible to effect a better dehydration to the hydrocarbon by raising the temperature of reaction and carrying it out in vacuo. Methyl-2-buten-3-*ol*-2, a tertiary unsaturated alcohol, might react in a similar manner to give isoprene as follows:

$$CH_3.C(CH_3)(OH).CH : CH_2 = CH_2 : C(CH_3).CH : CH_2 + H_2O.$$

Part II. Dehydration of Unsaturated Alcohols.

The dehydration of unsaturated alcohols, especially those containing a secondary and tertiary hydroxyl group, is usually effected by means of oxalic acid, potassium acid sulfate or acetic anhydride in the *wet* way.

Reif,[1] who studied the generation of divinyl hydrocarbons from alcohols of the buten-2-*ol*-1 type with a secondary hydroxyl group, states that he could not obtain the *dienes* by the dehalogenation of the chloro-esters of the alcohols, neither could he dehydrate these alcohols with acetic anhydride. Reif succeeded in dehydrating the unsaturated alcohols directly with potassium acid sulfate; but as this salt induces the partial polymerization of the hydrocarbons during the reaction, he effected the dehydration by using small quantities of the alcohols. In spite of this precaution, he could not obtain yields of the hydrocarbons higher than 15%. Abelmann,[2] on the other hand, discussing the dehydration of unsaturated alcohols, obtained by the interaction of tiglic aldehyde and organomagnesium compounds, has observed that the best way for producing the *dienes* is by dehalogenating the chloro-esters of the alcohols by means of quinoline. In some cases even potassium acid sulfate gave good results. Another method, which Abelmann discusses in the same paper is that of the action of hydrobromic acid in the use of Norris' esterification process. It has been mentioned above that unsaturated alcohols could also be changed to the butadiene-1,3 derivatives by distilling them over heated catalysts, preferably at reduced pressures. This method would be the simplest in many instances, as the yields of the hydrocarbons are very good.

Divinyl.—This is very easily obtained by carrying out the dehydration of buten-2-*ol*-1, $CH_3.CH : CH.CH_2OH$, at 400–450°.

Piperylene.—Penten-2-*ol*-4 was prepared by means of the Barbier-Grignard[3] reaction from crotonaldehyde and methyliodide. 130 g. of the alcohol were distilled over kaolin at 400–420° and 60–75 mm. A mixture of carbondioxide and ether was used as a freezing mixture for condensing the hydrocarbon. The water of dehydration amounted to 27 cc., theory calls for 27.5 cc. The crude organic product collected amounted to 75% of the theoretical. This was dried and fractioned through a column. The liquid on refractionation boiled at 41–44° and weighed 60 g. Reif[4] gives 40–41° as the boiling point of the hydrocarbon. The total high boiling residues from 130 g. alcohol used did not weigh more than 5 g.

It would seem that the decomposition of the alcohol was nearly theoretical. For a purer product the reaction must necessarily be carried out at lower pressures.

Hexadiene-2,4, $CH_3.CH : CH.CH : CH.CH_3$.—The alcohol[5] was prepared from crotonaldehyde and ethylmagnesium bromide. One hundred grams of hexenol were decomposed under the same conditions as the piperylene homologue. The hydrocarbon boiling at 78–82° weighed 40 g. The theoretical yield would be 72 g. Reif[1] gives the boiling point of this hydrocarbon as 80–82°; while, according to the "Lehrbuch,"[2] hexadiene-2,4 boils at 87–89°. The water of dehydration in this experiment amounted to 17 cc., instead of the theoretical 18 cc. Another sample of hexenol was decomposed at ordinary pressures. From 390 g. alcohol 190 g. of a liquid boiling between 76–86° was obtained. This was refractioned, and 145 g. of the hydrocarbon were collected at 80–84°. In the dehydration of pentenol and hexenol prepared from crotonaldehyde it is observed that there is always a fraction among the decomposition products, which boils below 30°, and has the smell of acetaldehyde. This latter substance is formed from the paraldehyde which is always present in the crotonaldehyde.

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[1] *Ber.*, 41, 2739 (1908).

[2] *Ibid.*, 43, 1574 (1910).

[3] *Ann. chim. phys.*, [7] 24, 465 (1901).

[4] *Ber.*, 41, 2744 (1908).

[5] Reif, *Ber.*, 39, 1603 (1906).

An attempt was made to dehydrate hexen-2-*ol*-4 by means of crystallized oxalic acid. Fifty grams of the alcohol were heated at 110° with 40–50 g. of the acid. The decomposition products were dried and fractioned as usual through a column. 7 g. of these boiled at 78 83°. Most of the hydrocarbon, however, was found in a polymerized condition floating over the oxalic acid. These polymerization products smelled strongly of terpene-like substances.

Conclusion.

Glycols and unsaturated alcohols can be dehydrated to divinyl hydrocarbons. The decomposition is improved by using reduced pressures during the pyrogenetic dehydration at temperatures above 350°.

Ditertiary α-glycols seem to be capable of dehydration to the *diene-1,3* hydrocarbons in presence of freshly reduced and finely divided catalytic metals. This reaction is made to take place at temperatures above 400°.

I would like to express, here also, my indebtedness to R. B. Earle for assisting me in these investigations.

CAMBRIDGE, MASS.

NEW PROCESSES FOR THE PREPARATION OF BUTADIENE-1,3 HYDROCARBONS. III. CATALYTIC DEHYDRATION OF HYDROXYL-COMPOUNDS.

BY L. P. KYRIAKIDES

Received March 4, 1914

Part I. Dehydration of Ditertiary Glycols.

Pinacone, a ditertiary α-glycol, has been subjected to a great many reactions which are characteristic of substances containing hydroxyl groups. Whereas this glycol[3] is quite stable when heated to fairly high temperatures in presence of alkaline compounds, such as a solution of sodium carbonate, it is very readily attacked by acids or dehydrating agents to give rise to pinacoline. The halogen-hydrin and the dihalogen esters of pinacone are more or less readily obtained by the action of the halides of phosphorus in the cold. The action of halogen acids, on the other hand, is dependent on the character of the acid, its concentration, the nature of the solvent and also on the temperature of reaction. Baeyer[1] has obtained the dibromide by treating anhydrous pinacone with a saturated solution of hydrobromic acid in acetic acid. Kondakoff[2] has prepared the dichloroester by treating the glycol at ordinary temperatures with an aqueous solution of hydrochloric acid saturated at —20°; or by saturating pinacone at —10° with hydrochloric acid gas and leaving the reaction mixture at ordinary temperatures for several days. In every instance, however, there is an appreciable amount of pinacoline formed. Kondakoff observes also that there is less pinacoline formed "the more concentrated the hydrochloric acid used is, and the more carefully heating during the reaction is avoided." Harries[3] reports that, when a strongly cooled chloroform solution of anhydrous pinacone is saturated with dry hydrochloric acid gas, a quantitative separation of a crystalline substance takes place, which is very sensitive to the action of air. This substance was found to consist of the monohydrochloride of pinacone, an addition product, and is said to be very unstable, decomposing even at 55° with evolution of hydrochloric acid gas.

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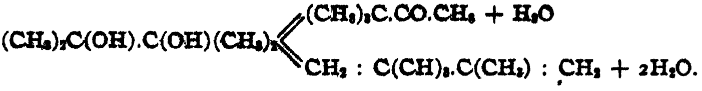
[1] *Ber.*, 41, 2744 (1908).

[2] Organ. Chemie, Meyer-Jacobson, 2nd ed., Vol I, Part I, pp. 887.

[3] Vorländer, *Ber.*, 30, 2266 (1897).

Dimethyl-2,3-butadiene-1,3, $CH_2 : C(CH_3).C(CH_3) : CH_2$.— Couturier[4] has observed that dilute sulfuric acid reacts with pinacone to give rise to small quantities of dimethylbutadiene, the main decomposition product being pinacoline.

Kondakoff[5] has carried out this reaction by heating pinacone with 10% sulfuric acid, and obtained, besides the two products mentioned by Couturier, also a fraction of high boiling point. The main reactions in Couturier's process take place as follows:



$$(CH_3)_2C(OH).C(OH)(CH_3)_2 \left\langle \begin{array}{l} (CH_3)_3C.CO.CH_3 + H_2O \\ CH_2 : C(CH)_3.C(CH_3) : CH_2 + 2H_2O. \end{array} \right.$$

Couturier[6] has also obtained the hydrocarbon in small quantities by heating pinacone with acetic anhydride in sealed tubes. Kondakoff,[7] on the other hand, prepared the same hydrocarbon by heating the dibromide of pinacone with alcoholic potassium hydroxide at 130–140°. These investigators have noted that β,γ-dimethyldivinyl is easily polymerized. Kondakoff,[1] furthermore, discovered that part of the hydrocarbon, after heating it at 150° for 5 hours with alcoholic potassium hydroxide, was polymerized to a product whose "properties remind one of those of rubber or of the polymers of styrol." The solid product "consists of a leather-like, elastic mass of an almost white color, which is not volatile with steam, is insoluble in water; but is soluble in hydrocarbons, ether and alcohol." In a later paper,[2] the same investigator reports briefly the results of further experiments on the polymerization of diisopropenyl. He sealed two samples of the hydrocarbon; one sample was prepared from pinacone by Couturier's sulfuric acid method, while the other was prepared by Kondakoff's own method by the dehalogenation of the dibromo-ester of pinacone with alcoholic potassium hydroxide. The former preparation had been fractioned over sodium. The tubes containing the hydrocarbon were left in diffused light for one year, at the end of which period both samples of the hydrocarbon were found to have solidified *completely*. Kondakoff states that the substance is amorphous and elastic like rubber, that it does not dissolve in the ordinary organic solvents, and only "swells up in benzol." He also mentions that the product obtained in this case must have been a higher polymerization product as compared with the one obtained by the action of alcoholic potassium hydroxide at 150°, hence the difference in solubility in the ordinary solvents. I have reproduced here the most important parts of Kondakoff's reports in support of his claim of having definitely proven that diisopropenyl at least could be made to polymerize to a rubber-like substance. Attempts have been made recently to discredit this claim of Kondakoff, on the ground that the products obtained by him are not to be regarded as true rubber, because the decomposition curves[3] of the diozonides of the "normal rubber" and the substance obtained by Kondakoff showed great variations. In justice, however, to Kondakoff be it said that he was able, as early as 1900, to observe a certain relation between his products and rubber, as there is undoubtedly some relation between them. It has been our experience that, with the possible exception of divinyl, the β,γ-dimethyl derivative seems to be the easiest to polymerize to a rubber-like substance by the action of heat and catalysts. By treating this hydrocarbon with 1% its weight of a catalyst and heating the mixture in metal receivers for three weeks at 100–115°, we have been able to obtain as high as 80% yield of a very tough and fairly elastic "rubber." The physical properties of this "rubber" vary considerably with the temperature and duration of polymerization, as would be expected.

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[1] *Ber.*, 26, 2563 (1893).

[2] *J. prakt. Chem.*, 62, 169 (1900).

[3] *Ann.*, 383, 183 (1911).

[4] *Ann. chim. phys.*, 26, [6] 485 (1892).

[5] *J. prakt. Chem.*, 62, 173 (1900).

[6] *Ann. chim. phys.*, 26, [6] 457–458 (1892).

[7] *J. prakt. Chem.*, 62, 170.

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[1] *J. prakt. Chem.*, 62, 175–176.

[2] *Ibid.*, 64, 109 (1901).

[3] Harries, *Ann.*, 395, 265 (1913).

The fairly high boiling point of dimethylbutadiene, its ease of polymerization, and its preparation from pinacone, which can itself be directly obtained by the reduction of acetone, make the study of the hydrocarbon both interesting and highly desirable. A great many patents have appeared during the last few years dealing with the dehydration of pinacone to the hydrocarbon. One of the most important of the processes,[1] patented by the Badische Anilin Fabrik of Germany, is the pyrogenetic decomposition of the glycol by dehydrating catalysts. A great many patents have been granted to the Elberfelder Farbenfabriken,[2] which are based on improvements of Couturier's method for the dehydration of pinacone in the wet way by heating it with dilute sulfuric acid. The chemists connected with this firm have discovered that the yields of hydrocarbon increase as the amount of the acid is diminished, in fact, by using traces of the acid they have been able to obtain as high as 70% of the theoretical yield of diisopropenyl. The same investigators have also generalized this observation so as to include the organic sulfonic acids. Furthermore, they have observed that acid salts of sulfuric acid such as potassium bisulfate, and normal sulfates which react acid, can also be used in effecting the dehydration of pinacone to the hydrocarbon.

In view of the work reported in this paper, the decomposition of glycols and alcohols to hydrocarbons in the wet way is not a simple dehydration in the usual sense of the expression in that it is produced by substances known generally as dehydrating agents, such as sulfuric, phosphoric and oxalic acids or zinc chloride. It is my belief that the dehydrations mentioned here are the result of a previous esterification, and are effected only by acids having a high ionization constant. Phosphoric and oxalic acids, weak acids,[3] which are usually spoken of as strong dehydrating agents, transform pinacone to pinacoline. Halogen acids, on the other hand, are not usually known as inducing the dehydration of alcohols or glycols. Being strong acids, they are well suited for esterification purposes, as is known to every one. These acids, as will be described soon, have been discovered to be capable of catalyzing hydroxyl substances to the hydrocarbons under certain conditions. These halogen acids, and especially hydrobromic and hydriodic acids, being susceptible of greater dissociation, are perhaps better adapted for the catalytic decomposition of pinacone to the hydrocarbon than straight sulfuric acid. It has been observed[4] that the halogen esters of pinacone are only obtained if the glycol is treated *in the cold* with concentrated halogen acids, and that warming of the liquid in presence of the excess of acid induces the formation of increasing quantities of pinacoline. We have discovered, however, that if pinacone is heated with very small amounts of any highly ionized acid, other than sulfuric acid and its derivatives, whose action was studied by the German chemists as noted above, the yield of hydrocarbon is very good. Acids, such as nitric acid which induce secondary reactions as oxidation, are not suited for the catalysis of hydroxyl compounds. The pinacone used in the following experiments was prepared by distilling the hydrate through a column until the temperature of the vapors attained 115°, and the residue was taken as practically anhydrous glycol.

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[1] D. R. P. 235,311; *Chem. Zentr.*, 1911, II, 112; Fr. Pat. 417,275; *C. A.*, 6, 2548 (1912). (The abstract in the *C. A.* needs correction. The French word "Alumine" has been translated "Aluminum" instead of *Alumina*—aluminum oxide.)

[2] U. S. Pat. 1,002,399, 1,002,400; *Chem. Zentr.*, 1912, II, 776, etc.

[3] Vorländer, *Ber.*, 30, 2266 (1897).

[4] Compare also Delacre, *Bull. soc. chim.*, [4] 3, 204 (1908).

Experiment 1.—Five hundred grams pinacone are put in a flask carrying a two-hole stopper one of which is fitted with a dropping funnel and the other with a fairly tall Young's column. The column is provided with a thermometer. The glycol is treated with 1–2 g. of hydrobromic acid solution (48%), and the mixture heated to boiling over a wire gauze. The heating is so regulated that the decomposition products distilling through the column do not register a temperature higher than 92°.

The reaction is carried out at constant concentration of the catalyst by dropping in fresh pinacone through the dropping funnel. This reaction lasts for quite a long time. In case it is observed to slow down, a fraction of a gram of hydrobromic acid is added and the decomposition of the glycol continued as long as desired. The slowing down of the reaction is due to the fact that some of the acid is gradually carried over by the distilling vapors, as was determined by testing the aqueous layer of the distillate. Two grams of the hydrobromic acid solution are capable of decomposing over 500 g. pinacone. The distillate is separated from the aqueous layer and the crystals of pinacone hydrate (pinacone is very volatile with steam) shaken twice with fresh water, dried over calcium chloride or potassium carbonate, and is finally fractioned through a column. The fraction boiling below 90° is refractioned, and the liquid boiling at 69–71° is collected as dimethyl-2,3-butadiene-1,3. The yield of hydrocarbon in this case was over 70% of the theoretical. The by-products of the reaction are mainly pinacoline, and a small amount of a liquid of high boiling point, which deposits big prismatic crystals on standing. The nature of the latter liquid and the crystals were not determined. *Hydrochloric acid* does not react well, which may be due to the relative ease with which it is volatilized, as can be proven by testing the distillate. In using this acid the reaction can be made to continue by the frequent addition of the acid, which, however, induces the formation of greater quantities of pinacoline. *Hydriodic acid* is as good a catalyst as hydrobromic acid. By treating 50 g. of pinacone with 5–7 drops of hydriodic acid solution, and carrying out the distillation of the decomposition products at constant concentration of the acid, I was able to obtain about 70% of the theoretical yield of dimethylbutadiene. *Trichloroacetic* acid is one of the strongest organic acids, its dissociation constant approaching that of the *strong* inorganic acids.

Experiment II.—Twenty-five grams of pinacone were put in a small flask, the apparatus being similar to the one used in Experiment 1, and the glycol decomposed by the action of about 1 g. trichloroacetic acid at 170–180°. The flask was heated in an oil bath. A good way to determine the amount of catalyst necessary to effect a fairly rapid decomposition is to heat the pinacone and to add the catalyst in small portions until a smooth reaction sets in, care being taken to avoid introducing an excess of the catalyst, otherwise the tendency will be in the direction of the formation of pinacoline.

The decomposition products, in this case, distilled over at about 90°. The reaction was not of long duration, hence I had to add fresh trichloroacetic acid at frequent intervals. The decomposition of 25 g. pinacone required about 4 g. of the acid. The action of trichloroacetic acid may be due to the hydrochloric acid set free by the decomposition of the organic acid at the relatively high temperature of reaction. This view is supported by the fact that testing the water of dehydration with silver nitrate gave a flocculent precipitate, which was evidently silver chloride. The purified hydrocarbon amounted to about 50% of the theoretical.

The fact that highly ionized acids induce the decomposition of pinacone in the wet way to the hydrocarbon has led us to assume that the salts of these acids with weak alkaline substances would react similarly. It is a matter of general knowledge that such salts react acid. It would follow, therefore, that the acid liberated after dissociation would play the role of catalyst. The weaker the base in combination with the acid, the more active will the salt be. Among such salts might be mentioned the aniline salts of the halogen acids. Nernst,[1] in a table of the affinity constants of the weak bases, gives the constant for the aniline base—$NH_3(C_6H_5)OH$—as $K10^6 = 0.00011$, as compared with ammonia, whose constant is given as $K10^6 = 23$. The affinity constants are directly proportional to the dissociation constants. It is evident that the aniline base is a much weaker base than ammonia, which is itself known as one of the weak bases. Because of this fact, the halogen acid salt of aniline reacts like the free acid.

Experiment III.—1.5 kilo pinacone were introduced in a 2-liter flask provided with a column and a dropping funnel. The glycol was then treated with about 20 g. aniline hydrobromide and decomposed by heating the flask on a wire gauze. The heating was regulated so that the vapors of the decomposition products registered a temperature of about 90° and the concentration of the catalyst was kept constant by dropping in fresh pinacone. Twenty grams of aniline hydrobromide were sufficient to catalyze more than 3 kilos of the glycol. The reaction can be continued indefinitely by adding small quantities of the salt or of the acid in case it is observed to slow down. This reaction is very smooth and ideal for laboratory as well as technical purposes. The distillate was treated as under Experiment I, and we obtained over 70% of the theoretical yield of dimethylbutadiene.

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[1] Theoretical Chemistry," English translation, 6th ed., p. 512.

Experiment IV.—Twenty grams of pinacone were heated and treated with small portions of anhydrous ferric chloride until a fairly smooth reaction had set in. It was found necessary to add fresh salt at frequent intervals, otherwise the reaction had a tendency to stop. Ferric hydroxide accumulated in the reaction flask, while the hydrochloric acid kept distilling over with the decomposition products. The purified hydrocarbon amounted to about 35%, the rest being mostly pinacoline.

Experiment V.—Twenty grams of pinacone were heated and treated gradually with small quantities of anhydrous aluminum bromide until the glycol began to be decomposed smoothly. The apparatus was similar to the one used in all these experiments. The reaction, as was expected, was found to be comparable with the straight hydrobromic acid catalysis. In this case aluminum hydroxide precipitates out of the reaction mixture. The decomposition was carried out as usual at constant volume by the introduction of fresh pinacone. In view of the above-mentioned behavior of the salts of the halogen acids with weak bases, it occurred to me that even some of the halogen esters of alcohols and glycols might act similarly. It is known, that the tertiary groups are characterized by their great mobility, and that the tertiary esters are easily hydrolyzed liberating the free acid; they also suffer partial decomposition at high temperatures, whereby the halogen acid is again set free.

Experiment VI.—Fifty grams pinacone were treated with a fraction of a cubic centimeter of trimethylethylene dibromide, which was freshly prepared by shaking it with a solution of sodium carbonate, drying and carefully fractioning *in vacuo.* The mixture was heated as usual, and the decomposition products worked up for the hydrocarbon. The yield of dimethylbutadiene was about 35%. It may be possible to regulate the relative quantities of these catalysts so as to obtain a maximum yield of the hydrocarbon. However, there is always a concentration of the catalysts below which no reaction takes place; while on the other hand, and this is true of the ditertiary α-glycols, when the concentration of the catalyst reaches beyond a certain maximum, the tendency is in the direction of pinacoline formation.

Part II. Dehydration of Secondary-Tertiary and Disecondary Glycols.

I. Methyl-2-pentadiene-2,4, $(CH_3)_2C : CH.CH : CH_2$.—This hydrocarbon is of especial interest, because it is, perhaps, the easiest of all the *divinyl* hydrocarbons to synthesize. Its physical constants are such as to make its handling a matter of the greatest simplicity. Comparing this hydrocarbon with its isomer dimethyl-2,3-butadiene-1,3, we find that the new hydrocarbon has a higher boiling point, and that its preparation is simpler and the yields more nearly quantitative. The starting point in the synthesis of both hydrocarbons is acetone. The new hydrocarbon is obtained as follows: Acetone is condensed to diacetone alcohol, the latter is reduced to the corresponding glycol, and this is finally dehydrated directly to the hydrocarbon. The yields in each step can be made very nearly quantitative. For the condensation of the ketone to diacetone alcohol see Hoffman,[1] and my paper on "Organic Preparations." Diacetone alcohol can be easily reduced to the glycol in a number of ways. By reducing it electrolytically we have obtained as high as 70% of pure glycol from a crude sample of diacetone alcohol. Zelinsky and Zelikoff[2] have reduced the ketone alcohol in fairly dilute aqueous solution with a 3% sodium amalgam, and have obtained 87% of the theoretical yield. The side-products formed in each step are comparatively small in amount. The reduction, on the other hand, of acetone to pinacone is not as readily effected. The electrolytic methods[3] do not give good results. The use of magnesium and aluminum[4] amalgams necessitates the increase in the cost of production, and the side products formed are appreciable in quantity. Besides, there is the problem of handling these side products, the working back of the metal oxides and the recovery of the mercury which necessarily would tend to make the process more complicated. There is also this point to be remembered, that the decomposition of pinacone is not as quantitative a reaction as that of its isomer, methyl-2-pentandiol-2,4. This latter glycol was used in the following experiment, and was prepared by the electrolytic reduction of diacetonealcohol.

Fifty grams of the glycol were catalyzed as usual by heating it with about 1 g. aniline hydrobromide. The mixture was heated at such a rate that the products distilling through the column registered a temperature below 95°. 240 g. more glycol were dropped in, and the decomposition finally carried to an end, until a few cubic centimeters only were left in the flask. The distillate was separated from the water, shaken twice with fresh water, dried over potassium carbonate and fractionated through a column. The fraction boiling below 90° (mostly 75–80°) was collected as hydrocarbon, and amounted to about 50% of the theoretical yield. The higher boiling fraction distilled over practically entirely between 110–135°, mostly above 125°, and, as will be seen later, consisted of an unsaturated alcohol. The hydrocarbon fraction was refractioned and the methylpentadiene was found to boil constant at 75.5–76.5°. As there is a possibility for the formation of the isomer, methyl-2-pentadiene-1,3, a small quantity of it may have been present in the hydrocarbon obtained above. This isomer, as will be described later on, boils at 76–77°, hence, the separation of the two hydrocarbons by fractional distillation is not possible. The dehydration of the methylpentandiol would have taken place as follows, with the first equation denoting, very probably, the course of the main reaction:

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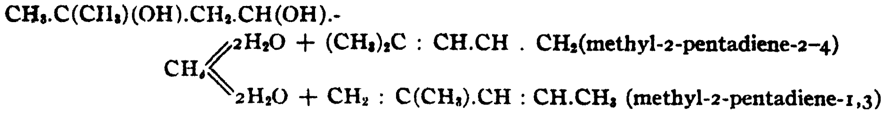
[1] THIS JOURNAL, 31, 722 (1909).

[2] *Ber.*, 34, 2858 (1901).

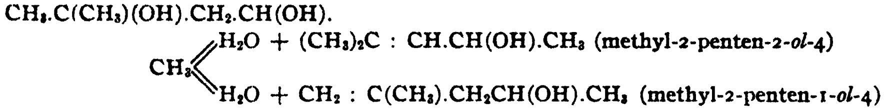
[3] Elbs and Brand, *Z. Elektrochem.*, 8, 783 (1902); *Chem. Zentr.*, 1912, II, 1756.

[4] D. R. P. 241,896; *Chem. Zentr.*, 1912, I, 176.



$$\begin{array}{l} CH_3.C(CH_3)(OH).CH_2.CH(OH).- \\ CH_3 \begin{array}{l} \nearrow 2H_2O + (CH_3)_2C : CH.CH\ .\ CH_2 \text{(methyl-2-pentadiene-2–4)} \\ \searrow 2H_2O + CH_2 : C(CH_3).CH : CH.CH_3 \text{ (methyl-2-pentadiene-1,3)} \end{array} \end{array}$$

That the first is the main reaction is supported by the general observation that there is more tendency for a tertiary hydroxyl to come off with a secondary rather than with a primary hydrogen atom. This is, for example, true of tertiary amyl alcohol, whose dehydration results in the formation of trimethylethylene; while only small quantities of the isomeric methylethylethylene ($CH_2 : C(CH_3).CH_2.CH_3$) are obtained. The reaction with the glycol would then proceed in two steps, the first step being the formation of the unsaturated alcohols as follows:



$$\begin{array}{l} CH_3.C(CH_3)(OH).CH_2.CH(OH). \\ CH_3 \begin{array}{l} \nearrow H_2O + (CH_3)_2C : CH.CH(OH).CH_3 \text{ (methyl-2-penten-2-}ol\text{-4)} \\ \searrow H_2O + CH_2 : C(CH_3).CH_2CH(OH).CH_3 \text{ (methyl-2-penten-1-}ol\text{-4)} \end{array} \end{array}$$

The high boiling fraction from the catalysis of methylpentandiol, boiling above 110° and amounting to about 50% of the theoretical yield of the glycol used, consisted, in all probability, mostly of methyl-2-penten-2-*ol*-4 with perhaps only small quantities of methyl-2-penten-1-*ol*-4.[1] As the glycol discussed here is not of the α-type, the quantity of the catalyst can be varied within fairly wide limits without any fear as to the course of the reaction. It can be said in general that the catalytic dehydration of ditertiary α-glycols is a much more sensitive reaction than that of the secondary-tertiary and disecondary β-glycols.

Glycols containing a primary hydroxyl, such as butandiol-1,3 cannot be dehydrated to the corresponding divinyl hydrocarbon by the methods described in this paper. This is undoubtedly due to the stability of the primary halide. These glycols are dehydrated to some extent giving rise to appreciable quantities of the unsaturated primary alcohols as follows:

$$HCR(OH)CHR.CH_2OH = HCR : CRCH_2OH + H_2O.$$

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[1] There is a possibility for the formation of two other isomeric unsaturated alcohols with a tertiary hydroxyl group. However, as tertiary hydroxyl groups are much more mobile than the secondary, the quantities of these tertiary alcohols would be insignificant even if present. All four isomeric alcohols would give, on dehydration, the two hydrocarbons which are discussed above, and none other.

I have also tried to dehydrate trimethylethylene glycol—$(CH_3)_2C(OH).CH(OH).CH_3$—a tertiary-secondary α-glycol, in a similar manner to isoprene, but the results were of a negative nature.

Polymerization of Methyl-2-pentadiene-2,4.—Several cubic centimeters of the dry hydrocarbon were introduced in a sealing tube and treated with a few pieces of sodium. The air in the tube was displaced by carbon dioxide, the tube was sealed and left in the steam bath. After two days the liquid was found to have solidified. This solid substance was treated according to the directions of Harries,[1] and was found to have rubber-like properties. This fact would be in support of the assumption that the hydrocarbon had conjugated double bonds.

II. Dehydration of a disecondary β-glycol.—The simplest representative of a disecondary β-glycol is pentandiol-2,4-$CH_3CH(OH).CH_2.CH(OH)CH_3$. This substance is very easily obtained by the electrolytic or amalgam reduction of hydracetylacetone, $CH_3.CH(OH).CH_2.CO.CH_3$.

Piperylene-pentadiene-2,4.—Twenty grams pentandiol were treated with about 1 g. hydrobromic acid solution, and decomposed as above described. The reaction was carried out by the addition of fresh glycol, and small amounts of the acid, whenever the reaction was observed to slow down. The catalysis was discontinued when the distillate amounted to about 60 cc. This was separated from the water of dehydration, shaken twice with a little cold water, dried over potassium carbonate and fractioned through a Young's column. Twenty-five cc. of the liquid distilled over below 60°, while the residue amounted to 18 cc. This residue boiled between 115–125°, and consisted evidently of pentene-2-*ol*-4, the partial dehydration product of the glycol. Grignard[2] gives the boiling point of this unsaturated secondary alcohol as 120–122°. The crude hydrocarbon fraction boiling below 60° was refractioned, and the hydrocarbon collected as piperylene boiling at 42.5–45°, mostly 43–43.5°, amounted to 18 g. It is seen that the yield of the hydrocarbon was at least 50%. The yield can probably be increased by a careful study of the conditions of catalysis.

It is evident now that ditertiary, tertiary-secondary and disecondary glycols, with the exception of the α-isomers in the last two cases, can be dehydrated to the corresponding divinyl hydrocarbons by the catalytic action of small quantities of halogen acids or their derivatives, which on dissociation liberate these acids. The mechanism of these reactions may be explained simply by the following equations:

$$(CH_3)_2C(OH).CH_2.CH(OH)CH_3 + HX = (CH_3)_2CX.CH_2CH(OH).CH_3 + H_2O.$$

$$(CH_3)_2CXCH_2CH(OH).CH_3 = (CH_3)_2C : CH.CH(OH)CH_3 + HX.$$

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[1] *Ann.*, 383, 217 (1911).

[2] *Ann. chim. phys.*, [7] 24, 465 (1901).

This reaction explains the presence of the considerable quantities of the unsaturated alcohols among the decomposition products of the glycols. Part of this unsaturated alcohol is esterified and subsequently dehalogenated to the hydrocarbon. As the water formed in the reaction keeps distilling over with the hydrocarbon and some of the alcohol, it could not play a prominent part in influencing the course of the reaction. The last steps in the dehydration of the glycol may then be represented as follows:

$$(CH_3)C : CH.CH(OH).CH_3 + HX = (CH_3)_2C : CH.CHX.CH_3 + H_2O.$$

$$(CH_3)_2C : CHCHX.CH_3 = (CH_3)_2C : CH.CH : CH_2 + HX.$$

This course of the reaction is supported by the observations of Charon[1] on the reactivity of the hydroxyl of crotonyl alcohol. Charon observed that buten-2-*ol*-1 is very easily esterified by the halogen acids, even in the cold, and that these same acids, contrary to their usual action, did not have any appreciable tendency to add at the double bond. In fact, the reactivity of the hydroxyl group is such that the esterification "is almost immediate, reminding one of the precipitation of a salt" and that the reaction " is much more easy and energetic than in the case of the corresponding saturated compounds." These derivatives of the alcohols are fairly unstable, reminding one of the halogen derivatives of carboxylic acids. "These facts are due to the electronegative character of the molecule, and it must be remarked that this character is much more accentuated for the *propenyl* group—$CH_3.CH : CH$—than for the vinyl group—$CH_2:-CH$." In crotonyl alcohol the hydroxyl group and the double bond are in the β-position to each other, which is also true of the unsaturated alcohols discussed in this paper, with this difference that the halogen esters formed in the latter case, being derivatives of secondary and tertiary alcohols, would be less stable at the temperature of reaction, and hence they are readily dehalogenated to the corresponding diethylenic hydrocarbons. This reasoning would probably be true in considering the mechanism of the dehydration of ditertiary α-glycols, where the partial dehydration product would be of the type of dimethylisopropenylcarbinol, $(CH_3)_2C(OH).C(CH_3) : CH_2$. In this case, however, because of the molecular structure, part of the alcohol may be metamerized to pinacoline under the influence of the acid reacting catalyst. That dimethylisopropenyl carbinol would be dehydrated to the hydrocarbon is made evident by the observation of Mariutza,[2] who obtained the hydrocarbon by heating the alcohol on the water bath with very dilute hydrochloric acid (0.1%). It would be interesting to know if Mariutza obtained any pinacoline in this reaction, as there is no mention made of the formation of other definite substances.

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[1] *Compt. rend.*, 128, 736 (1899).

[2] *J. Chem. Soc.*, 58, 728 (1890).

Part III. Dehydration of Unsaturated Alcohols.

Methyl-2-pentadiene-2,4.—The unsaturated alcohol used in this reaction was that obtained by the partial dehydration of methyl-2-pentadiol-2,4. It has been noted above that the catalysis of this glycol results in the formation of approximately equal quantities of the hydrocarbon and the alcohol. The boiling point of this alcohol, $(CH_3)_2C : CH.CH(OH).CH_3$, was found to be 130°. It is not necessary to purify the alcohol in case it is obtained from the glycol. The residue from the hydrocarbon, boiling above 110°, is dehydrated directly in the usual form of apparatus described above. Twenty-five grams of methylpentenol are treated with about 0.5–1 g. hydrobromic acid solution (aniline hydrobromide can be used with very good results) and the decomposition carried out at such a rate that the vapors distil over below 95°. Fresh alcohol is dropped in and the reaction continued as long as desired with the addition of small amounts of the catalyst in case the reaction slows down. The distillate is treated as under the glycol and the hydrocarbon purified by fractional distillation. The higher boiling fractions containing unchanged alcohol are catalyzed again. By repeating this process it is possible to decompose the unsaturated alcohol almost quantitatively to the hydrocarbon. As the alcohol was obtained from methyl-2-pentandiol-2,4, it follows that the dehydration of the glycol can be made nearly quantitative. I would mention here, that the hydrocarbon (see under the glycol) was polymerized by Harries' sodium process to a rubber-like substance.

Methyl-2-pentadiene-1,3, $CH_2 : C(CH_3).CH : CH.CH_3$.[1]—This hydrocarbon was mentioned in the discussion of the catalytic dehydration of methyl-2-pentandiol-2,4. It was observed that this isomer of methyl-2-pentadiene-2,4 might have been formed in small quantities in the decomposition of the glycol. The unsaturated tertiary alcohol used in this experiment was obtained, as noted in a previous paper, by the interaction of methylmagnesiumiodide and ethylideneacetone. The catalysis was carried out as usual using 0.2–0.4 g. of aniline hydrobromide in dehydrating 40 g. of the alcohol. This amount of the salt would have been sufficient to decompose much greater quantities of the alcohol, had it been necessary to do so. The reaction in this case, as in the last, was extremely easy and smooth. The distillation of the decomposition products took place below 85°. The distillate was treated as usual, and fractioned through a column. 70% of the liquid distilled over below 85°, mostly at 76–79°. This was refractioned and the hydrocarbon was found to boil at 76–77°. The residue, about 30%, was found to consist of the unchanged alcohol, and was dehydrated again. The total residue from this reaction that resisted dehydration did not amount to more than 1 g., and was found to consist of methylisobutylketone, which had been formed in the preparation of the alcohol in the Barbier-Grignard reaction.[1] The dehydration of the alcohol took place, most probably, according to the following equations:

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[1] Harries (*Ber.*, 34, 301–302) reports that he obtained this hydrocarbon by heating the phosphate of $(CH_3)_2C(NH_2).CH_2.CH(CH_3)NH_2$. He gives its b. p. as 75–77°. As the diamino compound is a derivative of methyl-2-pentandiol-2,4, if the discussion of the mechanism of the dehydration of the glycol holds true in the case of the diamino compound, the hydrocarbon of Harries must have been of the same nature as that obtained from the glycol, and must have consisted to a greater extent of methyl-2-pentadiene-2,4.

$$CH_3.CH : CH.C(CH_3)_2(OH) + HX = CH_3.CH : CH.C(CH_3)_2X + H_2O.$$

$$CH_3.CH : CH.C(CH_3)_2X = CH_3.CH : CH.C(CH_3) : CH_2 + HX.$$

Gry[2] states that the hydrocarbon obtained by him from the same alcohol by the action of acetic anhydride or acetylchloride, and boiling at 76–79°, "precipitates mercuric chloride in an aqueous solution, it is therefore probably, an allene, and must consequently possess the formula CH_3-$CH : C : C(CH_3)_2$; it would be therefore identical with trimethylallene of Ipatieff." Ipatieff[3] obtains the latter hydrocarbon, as is usual with such compounds, by the dehalogenation of methyl-2-bromo-3-penten-2, by heating this substance with alcoholic potassium hydroxide at 150°. The reaction took place as follows: $(CH_3)_2C : CBr.CH.CH_3 - HBr = (CH_3)_2C : C : CH.CH_3$.

In every instance where the dehydration of *unsaturated alcohols* to diolefines has been studied, it has been observed that the hydrocarbons contain conjugated double bonds. I do not know of a single case where it has been conclusively proven that the hydrocarbon obtained was not of the butadiene-1,3 type. The fact that a number of hydrocarbons obtained from the glycols and the alcohols mentioned in this paper were capable of polymerization to rubber-like masses, together with the observations of Reif,[4] Abelmann,[5] etc., force me to believe that the hydrocarbon obtained in this experiment also was none other than the divinyl derivative.

Isoprene.—About 10 g. methyl-3-buten-1-*ol*-3, $(CH_3)_2C(OH).CH : CH_2$, were treated with about 0.5 g. aniline hydrobromide, and the decomposition carried out as usual. Fifteen grams more of the alcohol were gradually dropped in, and the reaction continued until finally about 3 cc. of a liquid were left in the reaction flask. This liquid consisted mostly of the water of dehydration; while the insoluble organic layer was less than 1 cc. The catalysis was very smooth, and the reaction products distilled over below 80°. This reaction does not seem to induce any appreciable dimerization of the hydrocarbon, as is the case when the alcohol is treated with the usual "dehydrating" acids, such as oxalic and phosphoric acids. The decomposition products were dried over potassium carbonate and submitted to fractionation. Half of the liquid boiled constant at 35.5°, while the rest distilled over mostly at 97°, leaving practically no residue boiling above 100°. It is evident, therefore, that this high boiling fraction consisted of the unchanged isoprene alcohol, which was used over again. The side products are very little in amount, and may be due to impurities in the methylbutenol used. The fact that the hydrocarbon boiled constant at 35.5° is evidence of the purity of the isoprene.

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[1] See my paper on "Barbier-Grignard reactions."

[2] *Bull. soc. chim.*, [4] 3, 379 (1908).

[3] *J. prakt. Chem.*, 59, 535 (1899).

[4] *Ber.*, 41, 2739 (1908).

[5] *Ibid.*, 43, 1574 (1910).

Sodium isoprene rubber.—The hydrocarbon obtained as isoprene was treated in a small bottle with a few pieces of sodium, and left at room temperatures in diffused light, after stoppering well the bottle. The hydrocarbon soon began to show signs of thickening and contraction, and within one week was found to have solidified. The bottle was then heated at 60° for several hours, and its contents were immediately afterwards treated according to the directions of Harries.[1] We thus obtained a good yield of a tough and elastic rubber-like substance.

As both tertiary and secondary unsaturated alcohols are catalyzed to the corresponding diethylenic hydrocarbons, it is to be assumed that even methyl isopropenyl carbinol, treated as above with small quantities of a catalyst, will be decomposed to isoprene as follows:

$$CH_2 : C(CH_3).CH(OH).CH_3 + HX = CH_2 : C(CH_3).CHX.CH_3 + H_2O.$$

$$CH_2 : C(CH_3).CHX.CH_3 = CH_2 : C(CH_3).CH : CH_2 + HX.$$

There is a German patent,[2] assigned to the Elberfelder Farbenfabriken, which deals with the preparation of isoprene from methylisopropenyl carbinol. The reaction is carried out by treating the carbinol "with *dehydrating agents*, such as potassium bisulfate, mineral acids, zinc chloride, anhydrous oxalic acid, etc." The examples given comprize heating the alcohol with oxalic acid, distilling it over potassium bisulfate, and treating it in the cold with phosphorus pentachloride. It is known[3] that these methods seldom give very good results. In every case there is more or less di- and poly-merization of the hydrocarbon formed.

The processes described in this paper are entirely new, never used before in the dehydration of glycols or unsaturated alcohols to butadiene-1,3 hydrocarbons. The only cases that might be taken as somewhat similar are two: the first case relates to the dehydration by Mariutza[4] of dimethylisopropenylcarbinol, a tertiary alcohol, which was carried out by boiling the carbinol with very dilute aqueous hydrochloric acid (0.1%). The second case is that reported by Abelmann,[1] who observes that in attempting to esterify the unsaturated alcohols, obtained by the interaction of tiglic aldehyde and organomagnesium compounds, by Norris's[2] method using hydrobromic acid, he obtained the hydrocarbon instead. The esterification method of Norris consists in heating one part of the alcohol with 2–3 parts of the equivalent amount of a constant boiling mixture of hydrobromic acid and water. This means that the reaction being carried out in presence of a large excess of the acid, the hydrocarbons obtained by Abelmann will be partly acted upon by the acid to give rise to brominated derivatives. In fact, although Abelmann obtained a fair yield of the divinyl hydrocarbon, he states "the drawback of this method consists in that the hydrocarbon is made impure to a greater or less degree by bromides or even bromine, the complete elimination of which offers certain difficulties." From the final yield of the purified hydrocarbon which he obtains (60%), it is easy to see that the process of Abelmann is far from being ideal By means of the processes I have described in this paper it is possible to obtain a very pure hydrocarbon by a simple fractionation. The by-products consist practically entirely of the unsaturated alcohols, which can be dehydrated likewise to the hydrocarbon, so that the final yield of the hydrocarbon, in most cases, approximates the theoretical. The amount of catalyst used is in most cases insignificant as compared with the quantity of substance dehydrated. The method described above is not operative in the case of unsaturated primary alcohols, which behavior is due to the fact that the primary esters are stable at the temperatures of reaction.

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[1] *Ann.*, 383, 217 (1911).

[2] Ditmar, "Die Synthese des Kautschuks," p. 70; *J. Soc. Chem. Ind.*, 30, 1230 (1911); *C. A.*, 6, 2554 (1912).

[3] Reif, *Ber.*, 41, 2743; Abelmann, *Ibid.*, 43, 1577.

[4] *J. Chem. Soc.*, 58, 728 (1890).

Part IV. Dehydration of Saturated Tertiary Alcohols.

Although this chapter, properly speaking, does not come under the heading of *butadiene-1,3 hydrocarbons,* I take the liberty to insert it here, because of the similarity in the processes used. The success in dehydrating glycols and unsaturated alcohols, led me to consider the possibility of a similar catalysis of saturated alcohols in the wet way. Tertiary alcohols are distinguished from the primary and secondary alcohols by the comparatively greater reactivity of their hydroxyl group. Among the known methods[3] for the generation of olefines by the direct dehydration of alcohols in the wet way, we have the reactions which consist in heating the alcohols with dehydrating agents, such as sulfuric, phosphoric and oxalic acids, zinc chloride, etc. Tertiary alcohols are known to suffer dehydration in many esterification processes. Thus, when dimethylisopropyl carbinol, $(CH_3)_2C(OH)CH(CH_3)_2$, is made to react with acetic anhydride in presence of a few drops of concentrated sulfuric acid or a little zinc chloride, it is dehydrated to a mixture of unsaturated hydrocarbons, tetramethylethylene, and methylisopropylethylene. Tertiary amyl alcohol[1] is also easily dehydrated to the olefine by the action of a solid organic acid and phosphoric acid. The best method known is that of heating the tertiary carbinol at 60–70° with oxalic acid. The hydrocarbon obtained in this way is said to be pure trimethylethylene. Kondakoff,[2] on the other hand, states that the hydrocarbon obtained by the dehydration of tertiary amyl alcohol, always contains some of the isomeric methylethylethylene, $CH_2 : C(CH_3).CH_2.CH_3$. Wolkoff[3] in a report on the action of acids and their esters on alcohols at high temperatures, refers to the unfinished work of Bugajeff, in which the latter observed that very small amounts of any acid or ester induced the dehydration of secondary butyl alcohol to β-butylene. Wolkoff, on the basis of Bugajeff's observation, undertook the systematic study of the alcohols and discovered that secondary alcohols when heated in sealed tubes to above 200°, either alone or in presence of small amounts of acetic acid and its derivatives, did not suffer any change. On the other hand, if secondary and tertiary alcohols were heated to a little above 200° in presence of traces of a halogen acid or a halogen ester, they were decomposed completely to the corresponding hydrocarbon and water. Hydriodic acid and methyliodide were found to be the best agents to effect this dehydration. Tertiary alcohols naturally reacted more violently than secondary alcohols. Primary alcohols when heated with methyliodide were etherified.

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[1] *Ber.*, 43, 1577–1578, 1587 (1910).

[2] *Am. Chem. J.*, 38, 632 (1907).

[3] "Lehrbuch," Meyer-Jacobson, 2nd ed., part I, pp. 816, 817, 819.

The action of halogen acids on alcohols at their boiling point is that of esterification. Norris,[4] in the paper previously alluded to, observes that, when tertiary butyl alcohol is made to react with concentrated hydrochloric acid in the cold, the chloro ester is formed in quantitative yield. The corresponding bromo- and iodoesters are obtained if the tertiary alcohol is heated with an excess of the constant boiling mixtures of the hydrobromic and hydriodic acids with water. As far as is known to me, there is no indication in the literature that tertiary alcohols can be dehydrated by the action of halogen acids or their derivatives at temperatures below 200°. According to my discovery, saturated tertiary alcohols can be dehydrated similarly to the glycols and unsaturated alcohols.

Trimethylethylene, $(CH_3)_2C : CH.CH_3$. *Experiment I.*—The apparatus used was similar to the one described in Experiment I of Part I. Fifty grams of dimethylethylcarbinol were treated with about 3 cc. hydriodic acid solution, boiling at 125°, and the mixture heated over a wire gauze. The decomposition products distilling through the column showed at first a temperature of about 50°, which was evidently due to the fact that the distilling products consisted mostly of the hydrocarbon. As the accumulation of the water of dehydration progressed, the temperature of the vapors increased and water and some alcohol began to come over. The highest temperature registered by the vapors was 80°. The reaction was continued by dropping in fresh alcohol. The distillate was separated from the water, dried over potassium carbonate, and fractioned through a column. The fraction boiling below 50°, and amounting to over 50% of the dried product, was refractioned, and the liquid boiling at 36–40° was collected as trimethylethylene. The higher boiling fractions consisted entirely of the unchanged tertiary alcohol and could be used over again. The dehydration of dimethylethylcarbinol can therefore be made quantitative by this process. The only products left in the flask consist of traces of iodide which can be used to catalyze more of the alcohol.

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[1] *Ber.*, 26, Ref. 342 (1893).

[2] *J. prakt. Chem.*, 54, 454 (1896).

[3] *Chem. Zentr.*, 1890, II, 41.

[4] *Am. Chem. J.*, 38, 631, 632 (1907).

Experiment II.—Fifty grams of the carbinol were treated with 4 g. aniline hydrobromide and 2 cc. of a concentrated solution of hydrobromic acid. The reaction was carried out as in the last experiment, and the highest temperature registered by the vapors of the decomposition products was 75°. Fresh alcohol was dropped into the flask and the catalysis continued for quite a long time. The pure hydrocarbon obtained amounted to about 50%, while the rest of the products consisted of unchanged alcohol. The reaction in both experiments was very smooth and regular, and it is in my opinion the best process for preparing the hydrocarbon. Other tertiary alcohols, and *possibly* secondary alcohols having a high boiling point, would react similarly. The hydrocarbon obtained in the last two experiments is undoubtedly trimethylethylene, containing, very probably, small quantities of the isomeric methylethylethylene, as noted by Kondakoff.[1] The reaction may be said to have proceeded as follows:

$$(CH_3)_2C(OH).CH_2.CH_3 + HX = (CH_3)_2CX.CH_2.CH_3 + H_2O$$

$$(CH_3)_2CX.CH_2CH_3 = (CH_3)_2C : CH.CH_3 + HX$$

$$[(CH_3)_2CX.CH_2.CH_3 = CH_2 : C(CH_3).CH_2.CH_3 + HX]$$

Discussion of Results.

In this and the preceding two papers, I have reported on some new processes for the preparation of butadiene-1,3 hydrocarbons.[2] Among these, those discussed in this paper are by far the simplest. Whereas in the pyrogenetic catalyses the yields of the hydrocarbons may be made to approximate the theoretical, still the processes are quite complicated. The tendency of the butadiene hydrocarbons to decompose at the high temperatures of reaction would necessitate the use of vacuum, which would complicate the process still further. In this latter instance, it would be necessary to use refrigerating agents or other mechanical devices for avoiding the loss of valuable hydrocarbon. If, on the other hand, the pyrogenetic decomposition is carried out at ordinary pressures, the hydrocarbons will have to be purified by chemical means. The catalytic methods in the wet way can be carried out in the simplest form of apparatus, with practically no loss of hydrocarbon, with the further advantage that the latter can be freed from the accompanying *only* impurity—the unsaturated alcohol—by fractional distillation. Furthermore, the quantity of catalyst used is, as a rule, so small in comparison with the amount of substance catalyzed, that these catalyses in the wet way may be spoken of as being ideal from every point of view. There is one point, however, in which the pyrogenetic methods are superior to the wet methods, and that consists in the more general nature of the former. The oxides, secondary-tertiary and disecondary α-glycols, glycols having a primary hydroxyl group, as well as unsaturated primary alcohols cannot be catalyzed to the corresponding butadiene-1,3 hydrocarbons in the wet way. The decomposition of these substances, as already described, can be successfully carried out by the pyrogenetic catalytic methods.

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[1] *J. prakt. Chem.*, 54, 454 (1896).

[2] It is very probable that hydrocarbons containing more than two conjugated double bonds can be prepared from *similarly constituted* hydroxyl compounds, having already in the molecule one or more double bonds.

The preparation of the hydrocarbons directly from the hydroxyl compounds is the simplest of all known methods. The use of the quaternary ammonium derivatives, the chlorhydrins, or the dihalogen substitution products of these hydroxy-compounds, the unsaturated halides, etc., complicate the processes needlessly. I believe that I have indicated the lines along which work will be done in the future for the *commercial* preparation of the hydrocarbons in the synthesis of "rubber." This problem will eventually be solved, although it will require a good many years of earnest and patient study. The starting point in these syntheses will most probably be alcohol, which can be produced fairly cheaply.

Before concluding my reports on the work we have carried out in the synthesis of the divinyl hydrocarbons, I would like to state that we have left much that we would have liked to have finished. We would have liked, for example, to have made analyses of every compound obtained, prepared the halogen derivatives of the hydrocarbons for a better characterization of them; and above all, we would have liked to have studied the chemical and physical properties of the different isomeric hydrocarbons. Being outside of a truly scientific institution, and being moreover driven by the desire to save something out of the mad rush for patenting every conceivable and inconceivable organic reaction in the synthesis of these hydrocarbons, such as is still going on, we had very little time left at our disposal for anything else.

And now, that fortune has decreed that I should relinquish, at least for the present, this most fascinating of organic investigations, I would state that I have tried to derive the most rational conclusions possible under the circumstances from the experiments described in this and the previous papers, and that I shall be ever ready to acknowledge any false conclusions I may have arrived at.' The processes described by me have simplified the problem of the preparation of the unsaturated hydrocarbons, and I hope that they will be made use of in the systematic study of this branch of organic chemistry which is still in a more or less chaotic[1] state.

In conclusion, I would like to express my indebtedness to my colleague, R. B. Earle, for many valuable suggestions, and to thank him again for his constant help in carrying out a good many of the experiments described in this and the previous papers.

CAMBRIDGE, MASS

THE PREPARATION OF ALLYL IODIDE.

BY RASIK LAL DATTA

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The preparation of large quantities of allyl amine for conversion into the nitrite, necessitated the preparation of still greater quantities of allyl iodide, since allyl amine was obtained from this through the isothiocyanate. The method used for the preparation of allyl iodide was the action of yellow phosphorus on iodine in glycerol. This method is attended with some difficulty, and hence it has engaged the attention of chemists who have published modifications of the method from time to time. On undertaking the preparation of the compound, the various methods were tried, but it was found that in no case had the real difficulties been overcome. After a series of careful experiments, a modified method was devised, in which, as will be shown later, the difficulties were reduced to a minimum, and by which the preparation could be completed smoothly and in a very short time. Behal[2] in order to obviate the use of yellow phosphorus, employed red phosphorus in conjunction with a solution of iodine in allyl iodide and glycerol. This method does not, however, come under our consideration.

Claus[3] described the preparation of this compound in detail for the first time. His results were confirmed by James.[4] Claus did not use carbonic acid gas in this method. The yield obtained was 220 g. of pure allyl iodide from 240 g. of iodine.

Later, Kanonikoff and Saytzeff published a modification of the method in which, by the use of carbonic acid during the preparation, the yield was improved to 1000 g. allyl iodide from 1000 g. of iodine and the preparation of large quantities at a time was made possible. As a result of incorrect observation, they stated, moreover, that by following the method of Claus, without the use of carbonic acid gas, the yield could not be raised over 700 g. allyl iodide from 1000 g. of iodine. That the yield stated by Claus can actually be obtained has been verified by me. Moreover, Kanonikoff and Saytzeff held that their method alone enabled one to operate with large quantities. Experiments show, however, that the method of Claus does not require operating on a small scale, but that as large a quantity can be taken in one operation as in the other method. It is necessary to point out that both the above methods are attended by the usual difficulties of preparing this compound.

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[1] This is especially the case with the higher members of the unsaturated hydrocarbon series, where the possibility for the formation of a number of isomers, and their presence in the products obtained in the reactions, make their identification quite difficult and highly desirable.

[2] *Bull. soc. chim.*, 47, 876 (1887).

[3] *Ann.*, 131, 58 (1864).

[4] *Ibid.*, 185, 191 (1877).

After a series of careful experiments, the following method is proposed. In it the use of carbonic acid gas is avoided altogether, and no difficulty is experienced, the operation is carried through smoothly and quickly, while the yield is equally satisfactory.

The first difficulty attending the method is that the addition of phosphorus is tedious and the addition of several grams takes hours. Moreover, the pieces which are added are not easily brought into interaction but must be stirred with a glass rod pushed through the tubulus of the retort. Sometimes, even on stirring, no action takes place for a considerable time; and if, in the belief that the action is over, more pieces are added before the previous portion has been used up the reaction may suddenly set in with explosive violence. Local warming with a flame is not safe. The following details have been found to give the most satisfactory results:

The apparatus consists of a retort, fitted with a funnel having a glass stopper. The retort is connected with a condenser and receiver as usual. The retort is kept dipped in a larger-sized water bath, which can be heated from beneath. Glycerol is next poured into the retort and then the iodine, taking care that all of it drops on the glycerol and that none sticks to the side of the retort. When all the iodine is added, the water bath is heated to boiling. A small piece of phosphorus is then added, the stopper of the funnel being removed temporarily. When this comes into contact with iodine in the hot glycerol, it reacts at once. As a result of the interaction, some allyl iodide is formed which takes up some iodine into solution. A second piece is immediately added and takes part in the reaction in like manner. On continuing the addition of larger pieces of phosphorus, more and more allyl iodide is formed, which, taking up increasing quantities of iodine into solution, facilitates the reaction. After a considerable quantity of phosphorus has been added in this manner, the allyl iodide formed distils off, being heated on the water bath and the heat generated by the reaction. Proceeding in this manner, after the addition of only a few grams of phosphorus (which takes but a short time), large pieces weighing as much as 3-4 g. can be added in quick succession. The operation can, therefore, be very smoothly and quickly completed. Since some isopropyl iodide (b. p. 89°) is invariably produced in this reaction, the mixture boils at less than 100° and, hence, the major part of the distillation is finished on the water bath. The last traces can be distilled off by heating with a constantly moving luminous flame. The allyl iodide is dried and purified in the usual manner.

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CHLORINATION BY MEANS OF AQUA REGIA. THE CHLORINATION OF BENZENE, THIOPHENE, TOLUENE AND MESITYLENE.

BY RASIK LAL DATTA AND FRANCIS V FERNANDES

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Although several processes have been used for the chlorination of organic compounds, there has always been difficulty in finding a method which could be carried out economically, both as regards the time and the chemicals. The only method which has been applied rather extensively is the one in which chlorine is passed through a liquid, usually in the presence of a carrier. In this case, however, the chlorination of a single compound means the work of some hours, not to speak of the trouble necessitated by the conditions demanded, *viz.*, the influence of direct sunlight, etc.

Some of the difficulties, mentioned above, seem to be obviated by the use of a mixture of nitric and hydrochloric acids as a chlorinating agent. Some investigators have used it in some oxidizing experiments, but they have pronounced it as an unsatisfactory reagent, chiefly owing to its exceedingly active properties. While this is true for some compounds, it has been found that the reagent in many cases acts as a powerful chlorinating agent, and in others both as an oxidizing and chlorinating agent. It acts as a simple chlorinating agent towards compounds which are not easily susceptible of oxidation with nitric acid, while, if the substance in question is susceptible of oxidation by nitric acid, both the processes of oxidation and chlorination occur simultaneously. In fact, the changes that can occur under any circumstances may be described thus: We know that a mixture of nitric and hydrochloric acids yields chlorine and nitrosyl chloride, the latter decomposing in the presence of water into nitrous fumes and hydrochloric acid. Hence, either or both of the following reactions may take place: first, the strong nitric acid may oxidize or nitrate the body coming into contact with it; and secondly, the nascent chlorine may unite with great energy with such compounds. In the case of hydrocarbons, generally, the reagent acts simply as a chlorinating agent, with the production of the several chloroderivatives, according to the conditions under which the chlorination is carried out. It might be thought strange that it does not act as a nitrating agent too. That this is not probable may be seen by the fact that chlorine has a greater influence than nitro group; and wherever there is any chance of substitution, the chlorine is first to take the place, because it is not only active in nature but it is also in the nascent state. Again, the chlorination with aqua regia becomes more vigorous than with ordinary reagents owing to the mere presence of nitric acid. Evidence in favor of this will be adduced later on, where it will be shown that the reagent achieves some substitutions which cannot be achieved by nascent chlorine alone in other processes.

Thus the nascent chlorine, obtained from a mixture of hydrochloric and nitric acids, affords a rapid method of chlorinating hydrocarbons in general. In addition to the rapidity and consequent economy of time, the ease with which the chlorination is carried out is a further advantage. It is only necessary to warm the hydrocarbons with the acid mixture with occasional shaking. In a very short time the hydrocarbon is chlorinated with the production of a chlorocompound, or a mixture of chlorocompounds where there is a possibility of the formation of more than one derivative. Generally, it is found that the method may be used to prepare a particular chloroderivative, as required, by varying the conditions of the experiment. It can, however, be laid down as a general rule that the longer the liquid is kept in contact with the acid mixture, the greater is the percentage of higher chlorinated products.

The chlorination of the following hydrocarbons has been effected:

Benzene.—It is well known that chlorine gas acts both substitutively and additively on benzene to form the various chloroderivatives. Benzene hexachloride is prepared by the interaction of chlorine on benzene in sunlight[1] or by passing chlorine through boiling benzene.[2] Other additive chloroderivatives of benzene can be prepared by varying the process a little and sometimes by the intervention of a little alkali. The substitutive chlorocompounds, especially the monochloro- and dichlorobenzenes, can be prepared by the chlorination of benzene in the presence of a little iodine.[3] In this case only two dichlorobenzenes, the *o*- and *p*-derivatives, are produced, the latter in predominating quantity.[4] Monochlorobenzene can also be prepared by chlorinating benzene with sulfur chloride,[5] or with sulfuryl chloride.[6] The whole series of the chlorocompounds of benzene has been exhaustively studied by Beilstein and Kurbatoff.[7]

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[1] Faraday, *Ann. chim. phys.*, [2] **30**, 274; Mitscherlich, *Pogg. Ann.*, **35**, 370.

[2] Lesimple, *Ann.*, **137**, 123; Heys, *Z. Chem.*, 1871, p. 293.

[3] Hasse, *Ber.*, **26**, 1053 (1893).

[4] Müller, *Jahresb.*, 1864, p. 524.

[5] Schmidt, *Ber.*, **11**, 1173 (1878).

[6] Dubois, *Z. Chem.*, 1866, p. 705.

[7] *Ann.*, **182**, 97 (1876); **192**, 229 (1878).

Later, the chlorination of benzene has been effected with ferric chloride with the production of monochlorobenzene.[1] Monochloro- or dichlorobenzene has been prepared by passing the calculated quantity of chlorine through a mixture of benzene and aluminium chloride heated to 50–55°.[2] By the method to be described here, both monochloro- and dichlorobenzenes could be prepared very easily and in a very short time.

100 cc. of benzene were mixed with 450 cc. of a mixture of concentrated hydrochloric and nitric acids (2 : 1) in a large flask. When the first action which generally takes place ceased, the flask was heated on the water bath with a reflux condenser for about an hour. The contents of the flask were well shaken from time to time during the progress of the reaction. The flask was then cooled, and the upper oily layer was separated from the acids below by means of a separating funnel. The oily liquid was washed several times with water, then with dilute alkali and finally again with water to remove all traces of free acids. After drying the oil with a few bits of calcium chloride, it was subjected to fractional distillation. For effecting the separation between the several chloro-compounds formed in the process, a two-bulb Würtz still-head was used. The distilling flask was heated on the wire gauze with a small flame. During the distillation the temperature rose very rapidly at first to 80°, at which temperature all the unchanged benzene passed over. Two fractions were collected: the first between 80–105°, and second between 150–172°. At 172° the temperature rise stopped abruptly and pure dichlorobenzene came over and solidified to thin, colorless leaflets, m. p. 53°. During the distillation of *p*-dichlorobenzene, the ordinary condenser was replaced by an air condenser. The remaining liquid in the flask charred after the distillation of *p*-dichlorobenzene was over. By refractionating the previous fractions, pure monochloro- and *o*-dichlorobenzenes were separated and the following products were obtained from 100 cc. of crude chlorinated product: Unchanged benzene, 50 cc.; monochlorobenzenes, 15 g.; *o*-dichlorobenzene, 4 g.; *p*-dichlorobenzene, 18 g.; charred liquid, 10 cc.

Hence, this method may serve as a convenient method of preparing both monochloro and *p*-dichlorobenzenes. The yield of *p*-dichlorobenzene could be increased by prolonging the chlorination process somewhat.

Thiophene.—Chloro derivatives of thiophene are prepared by passing chlorine through thiophene, whereby all the four chlorothiophenes are produced.[3] Monochlorothiophene can also be prepared by the interaction of thiophene and sulfuryl chloride in absolute alcohol.[4]

The chlorination of thiophene by aqua regia has been effected as follows:

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[1] Thomas, *Compt. rend.*, 126, 1212.

[2] Mouneyart, Pouret, *Compt. rend.*, 127, 1026.

[3] Weitz, *Ber.*, 17, 794 (1884).

[4] Töhl, Eberhard, *Ber.*, 26, 2947 (1893).

To a sufficient quantity of a mixture of nitric and hydrochloric acids in the proportion of 1 to 2, thiophene was added. A vigorous reaction ensued with the turning of the thiophene color into red passing transiently through a blue-black appearance. After several minutes the red liquid sank beneath the acid mixture, evidently on account of the increase of density of the liquid as a result of the formation of chlorothiophenes. The oil was separated from the acid mixture and treated with dilute alkali and water to free it from the acids. After drying it over calcium chloride, it was distilled and the following fractions were collected: (1) up to 100°; (2) 101–140°; (3) 141–180°; and (4) 181–205°. By repeating the fractionation twice over, the whole mixture was resolved into unchanged thiophene, monochloro-, dichloro- and trichlorothiophenes. The unchanged thiophene was about $^1/_3$ of the whole product, and the three chloroderivatives were obtained in almost equal quantities. It should be noted that the proportions of the different chloroderivatives vary with the duration of the reaction.

Toluene.—The chlorination of toluene has been effected with free chlorine sometimes in the presence of a carrier. The chlorine either enters the side-chain or the nucleus according to the conditions under which the reaction occurs. The chlorine enters the side-chain if toluene is chlorinated by boiling with phosphorus pentachloride as carrier. Some chlorotoluenes have also been prepared by heating toluene with ferric chloride, sulfuryl chloride, etc. The primary product of chlorination of toluene with aqua regia is benzyl chloride, the chlorine attacking the side-chain; besides that other chlorotoluenes are formed, the *o*-chlorotoluene being formed in predominant quantity. The other dichloro- and trichlorotoluenes which are invariably formed cannot be conveniently isolated.

The method followed in this case was exactly the same as the one used before, with the exception that the reflux condenser was dispensed with. The preliminary experiment was carried out with 30 cc. of toluene and 120 cc. of the mixture of acid (1 : 1). The liquid was heated on the water bath half an hour. The product was washed with alkali as usual, dried and fractionated with a still-head. The fractions were collected as follows: 20 cc. yielded (1) up to 132° ——; (2) 132–155° 3–4 cc. (in reality all this came over at 155°); (3) 155–180° 15 cc. (in reality all this came over at 175°).

Thus we find that benzyl chloride was the principal product of the reaction, *o*-chlorotoluene being formed in fairly good quantities. The chloroderivatives may, however, be prepared as desired by varying the conditions as is shown by the following experiment:

100 cc. of toluene were mixed with 600 cc. of the mixture of conc. HCl and HNO_3 (2 : 1) and heated on the water bath for one hour, 70 cc. of the crude product being obtained. On distilling the following fractions

were collected: up to 140°, 14 cc.; from 140–158°, 20 cc.; 158–168°, 11 cc.; 168–175°, 4 cc.; the liquid charred, 18 cc. By fractionating them again, the various pure chloroderivatives were obtained. Here we have *o*-chlorotoluene formed in predominating quantities and *p*-chlorotoluene is formed in tolerably good yield. Benzyl chloride is scarcely formed.

Mesitylene.—The chlorination of mesitylene has been effected by Fittig and Hoogewerff,[1] by passing chlorine through cold mesitylene when it acts vigorously with the formation of mono-, di-, and trichloromesitylenes. The chlorination of mesitylene by aqua regia has been found to be very satisfactory, and in about five minutes a mixture of the chloromesitylenes can be prepared.

Ten cc. of mesitylene were mixed with 50 cc. of conc. HCl and HNO_3 (2 : 1). The mixture was warmed on the water bath for five to ten minutes and was shaken nearly all the time. Oily drops were formed, which afterwards collected, on shaking more, into a thick viscous liquid. This was separated by decantation, and washed as described in the case of benzene, when it was obtained as a mass of soft, white crystals. This was next fractionally crystallized from alcohol to effect the separation of the different chloroderivatives formed, according to the procedure used by Fittig and Hoogewerff.

After a systematic fractionation, it was found that dichloromesitylene, $C_6HCl_2(CH_3)_3$, was formed in great quantity. Trichloromesitylene, $C_6Cl_3(CH_3)_3$, was produced in fairly large quantity while monochloromesitylene was scarcely formed in any significant quantity. It may be pointed out that besides the chloromesitylenes, no secondary products are formed.

We are at present engaged in systematically applying aqua regia as a chlorinating and oxidizing reagent and shall lay before the Society the results obtained from time to time.

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SIMULTANEOUS CHLORINATION AND OXIDATION BY MEANS OF AQUA REGIA. THE PREPARATION OF CHLOROANIL FROM *p*-PHENYLENEDIAMINE AND HYDROQUINONE.

BY RASIK LAL DATTA

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It was shown previously that aqua regia acts essentially as a chlorinating agent in cases where there is no possibility of oxidation, and as has been described before, the chlorination of hydrocarbons was effected with ease by means of this reagent. But in cases of chlorination where there is also the posibility of oxidation, both reactions occur rapidly. Now,

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[1] *Annalen*, 150, 323.

p-phenylenediamine is known to give chloroanil by simultaneous chlorination and oxidation, but only with great difficulty, repeated treatment with different reagents being necessary to attain the end desired. Since aqua regia acts both as a vigorous chlorinating and oxidizing agent, it is quite expected that this reagent would convert *p*-phenylenediamine into tetrachloroquinone with ease, and, in fact, this has been found to be the case. It has also been found that hydroquinone, which has hydroxy groups in the para position, is also readily chlorinated and oxidized, giving pure chloroanil.

Chloroanil is readily formed from organic compounds. Erdmann[1] obtained it by passing chlorine through an alcoholic solution of chloroisatin. It is also formed by the action of potassium chlorate and hydrochloric acid on a variety of substances. It has been obtained by this reagent from aniline, phenol,[2] salicylic acid, nitrosalicylic acid,[2] dinitrosalicylic acid,[3] tyrosin[4] and *m*-aminobenzoic acid.[5] Furthermore it is formed by the action of fuming nitric acid on perchlorophenol[6] and also on 1,2,4,5-tetrachlorobenzene.[7] It has been obtained from hexachlorobenzene by treatment with a mixture of nitric and sulfuric acids[8] and also from hexachlorophenol.[9]

Chloroanil is now prepared according to the method of Graebe,[10] by the action of potassium chlorate and hydrochloric acid on *p*-phenylenediamine. This method still prevails as the most satisfactory. A short summary of the process will indicate the trouble that has to be undergone and the reagents that have to be used to prepare a pure sample of the substance.

p-Phenylenediamine hydrochloride is suspended in water and to it coarse crystals of potassium chlorate are gradually added and then hydrochloric acid. The addition of chlorate takes a day and the temperature has to be maintained between 20–30°. The next day the mixture must be warmed on the water bath until all the chlorate is decomposed. The crude product which contains about 25% of trichloroquinone, is collected and washed. Then it must again be treated with hydrochloric acid on the water bath for 1–2 hours. After washing it is again oxidized with potassium dichromate and hydrochloric acid. Even then it is not obtained quite pure, but must be recrystallized from toluene in order to get a com-

[1] *Ann.*, **48**, 309.

[2] Hofmann, *Ibid.*, **52**, 57.

[3] Stenhouse, *Ibid.*, **78**, 4.

[4] Staedeler, *Ibid.*, **116**, 99.

[5] Erlenmeyer, *Jahresb. Chem.*, **1861**, p 404.

[6] Merz, Weith, *Ber.*, **5**, 460 (1872).

[7] Beilstein, Kurbatow, *Ann.*, **192**, 236.

[8] Israti, *Bull. soc. chim.*, [3] **3**, 184.

[9] Barral, *Ibid.*, [3] **11**, 705.

[10] *Ann.*, **263**, 6.

pletely pure product. It is, therefore, quite evident that a considerable amount of trouble has to be undergone to prepare pure chloroanil.

Preparation from p-Phenylenediamine.—The preparation of perfectly pure chloroanil from *p*-phenylenediamine can be effected very simply and in a very short time, by means of aqua regia, as follows: To 100 cc. of a mixture of nitric and hydrochloric acids (2 : 3), 15 g. of *p*-phenylenediamine hydrochloride are added and the substance is allowed to react, with occasional warming on the water bath. A very gradual change in the color of the substance is forthwith noticed, going through yellow-brown to bright yellow. Toward the end of the operation, the flask containing the acid mixture is left on the water bath continuously until all of the acid fumes are driven off and the transformation into chloroanil becomes complete. The product is next washed with water and dried. It consists of perfectly pure tetrachloroquinone, which sublimes completely without melting and leaves only a black stain in the subliming vessel. The sublimed product consists of fine yellow plates having a melting point of 290° in sealed capillary tubes. The yield obtained was 10 g. of chloroanil. It may sometimes happen, as a result of too rapid heating of the acid mixture, that *p*-phenylenediamine is not completely converted into chloroanil. In such cases, a fresh treatment of the resulting substance with a smaller quantity of acid mixture is necessary.

Preparation from Hydroquinone.—Hydroquinone, which is similar to *p*-phenylenediamine in structure, might be expected to yield chloroanil when similarly treated. Since hydroquinone has not as yet been treated with an oxidizing and chlorinating reagent, it was thought desirable to first test the possibility of formation of chloroanil from hydroquinone by the action of potassium chlorate and hydrochloric acid. For this purpose, hydroquinone is suspended in strong hydrochloric acid and to it potassium chlorate is gradually added, whereupon the substance turns yellow. The process is continued for sometime longer with fresh additions of potassium chlorate and warming on the water bath. After a considerable time, the product is found to consist of a mixture of the lower chloroquinones. Hence the mixture of potassium chlorate and hydrochloric acid is quite unable to transform hydroquinone completely into chloroanil.

Accordingly, hydroquinone was next treated with aqua regia similarly to *p*-phenylenediamine. By its action, the substance gradually turns more and more yellow until it is of a bright yellow color. The reaction is finished on the water bath, when it consists of a bright yellow substance which is pure chloroanil and can be sublimed quite completely without previous fusion. It gives a melting point of 290° in a sealed capillary tube as observed by Graebe.

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METHODS OF ESTIMATION OF SEMICARBAZIDE BY ITS INTERACTION WITH HALOGENS AND HALOGEN OXYACIDS.

BY RASIK LAL DATTA.

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The action of chlorine, and potassium chlorate and hydrochloric acid on semicarbazide has been taken up for study in order to ascertain the nature of the decomposition of the latter body. It was found that these reagents bring about the complete rupture of the semicarbazide molecule, with liberation of large amounts of nitrogen and carbon dioxide. Following this up, the action of other similar reagents was taken into consideration. These have been, bromine, bromic acid and iodic acid, the latter in the form of salt. It has been found that semicarbazide hydrochloride is decomposed by the above reagents, yielding an amount of nitrogen which always bears a certain invariable proportion to the total nitrogen of semicarbazide. These reactions, as will be shown later, could be used conveniently for the gasometric estimation of semicarbazide, for which no satisfactory method of estimation is as yet known. It is to be noted that the reagents named do not react with urea and, hence, the estimation of semicarbazide could be effected in the presence of this body.

Maselli[1] has given a round-about method for the estimation of semicarbazide. He utilizes the reaction that when semicarbazide is boiled with dilute acids, decomposition occurs with the quantitative separation of ammonia and hydrazine, according to the equation:

$$NH_2CO.NH.NH_2 + 2H_2O = NH_3 + CO_2 + H_2O + N_2H_4.$$

The quantity of semicarbazide can hence be estimated either (1) by determining the amount of hydrazine, by adding an excess of a standard solution of potassium iodate, boiling until all the iodine set free is removed, and titrating the excess of potassium iodate with standard sodium thiosulfate; (2) by determining the amount of ammonia formed, by adding sodium hydroxide and distilling the ammonia set free into a known volume of standard acid.

The action of semicarbazide upon the halogen oxyacids is interesting and varies progressively with the atomic weight of the halogens. Like carbamide, semicarbazide hydrochloride is completely decomposed by sodium hypochlorite or sodium hypobromite with the quantitative liberation of nitrogen. The action of potassium chlorate and hydrochloric acid is, however, quite different.

To a solution of semicarbazide hydrochloride in a Crum's nitrometer, a little powdered potassium chlorate and then strong hydrochloric acid is added. A vigorous reaction ensues with copious evolution of a gas consisting of nitrogen, carbon dioxide and chlorine. After washing down the excess of chlorine, the carbon dioxide was completely absorbed by strong alkali. The remaining gas was found to bear a constant ratio to the total nitrogen, namely, $^2/_3$ of the total. The reason for washing down the chlorine before the addition of alkali is that the alkali, in the presence of chlorine, acts as hypochlorite and, hence, instead of $^2/_3$, the total amount of nitrogen is liberated. So potassium chlorate and hydrochloric acid liberate only $^2/_3$ of the nitrogen according to the following equation:

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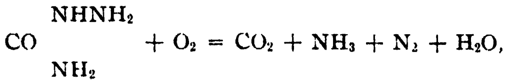
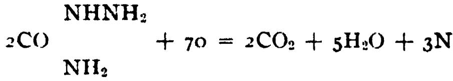
[1] *Gazz. chim. ital.*, 35, I, 267 (1905).



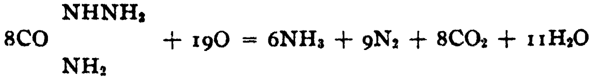
$$\mathrm{CO}\begin{matrix}\mathrm{NHNH_2}\\ \mathrm{NH_2}\end{matrix} + \mathrm{O_2} = \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{N_2} + \mathrm{H_2O},$$

while alkaline hypochlorite decomposes it quantitatively thus:



$$2\mathrm{CO}\begin{matrix}\mathrm{NHNH_2}\\ \mathrm{NH_2}\end{matrix} + 7\mathrm{O} = 2\mathrm{CO_2} + 5\mathrm{H_2O} + 3\mathrm{N_2}$$

The reaction between semicarbazide hydrochloride and potassium bromate is a little more energetic than the reaction with potassium chlorate and hydrochloric acid. When solid potassium bromate is added to solid semicarbazide hydrochloride and the mixture is moistened, a vigorous reaction instantly begins with the copious evolution of gas and bromine vapors. At the same time the mixture becomes intensely hot. But if the semicarbazide hydrochloride be in the form of a tolerably strong solution, a few seconds elapse before any sign of reaction is visible, after which, suddenly, a vigorous reaction ensues with the evolution of gas and liberation of bromine. The time required for the reaction to take its course depends upon the dilution of semicarbazide hydrochloride. In the case of somewhat dilute solutions, as long as 5 to 10 minutes elapses before the sign of any reaction is evident. When the dilution is very great no reaction takes place at all. But a little hydrochloric acid added to such a mixture starts up the reaction at once. If the reaction be carried out in a Crum's nitrometer with the help of a little hydrochloric acid, finally treating the resulting gas with alkali after washing down the excess of free bromine, the percentage of nitrogen comes out nearly $^3/_4$ of the total quantity present in semicarbazide. The reaction evidently takes place according to the equation:



$$8\mathrm{CO}\begin{matrix}\mathrm{NHNH_2}\\ \mathrm{NH_2}\end{matrix} + 19\mathrm{O} = 6\mathrm{NH_3} + 9\mathrm{N_2} + 8\mathrm{CO_2} + 11\mathrm{H_2O}$$

But if the alkali be added directly in the presence of bromine in the above reaction, it acts as hypobromite and quantitative liberation of nitrogen is the result.

The reaction of semicarbazide hydrochloride with potassium iodate is more energetic than that with potassium bromate. Potassium iodate interacts with semicarbazide hydrochloride in very dilute solutions with copious evolution of gas and liberation of iodine. On carrying through the reaction in a Crum's nitrometer, it is found that the nitrogen given out is $^{3}/_{4}$ of the total nitrogen. Hence there is noticeable a beautiful transition in the reactions of the halogen oxyacids towards semicarbazide. Potassium chlorate interacts only in conjunction with hydrochloric acid, setting free $^{2}/_{3}$ of the total nitrogen. Potassium bromate interacts without the help of any acid in moderately strong solutions and in the presence of acid in dilute solutions, liberating nearly $^{3}/_{4}$ of the total nitrogen. Potassium iodate interacts without the help of any acid at all dilutions, liberating just $^{3}/_{4}$ of the total nitrogen.

Chlorine and bromine decompose semicarbazide hydrochloride with the evolution of gas. The decomposition by means of chlorine could not be used as an analytical method since chlorine cannot be obtained in a good concentration suitable for carrying out such reactions.

When bromine water is added to semicarbazide solution in a Crum's nitrometer, copious evolution of gas takes place. On washing down the excess of bromine and absorbing the carbon dioxide generated by strong lye, the resulting nitrogen is found to be $^{3}/_{4}$ of the total, and the reaction is expressed by a similar equation given above in the case of potassium bromate and hydrochloride acid. But if, instead of washing down the excess of bromine, caustic alkali be directly added, the action is equivalent to that of alkaline hypobromite with the quantitative liberation of nitrogen.

The actual data of a few of the numerous experiments performed are given below:

I. With potassium chlorate and hydrochloric acid.

(*a*) Using alkali in the presence of chlorine, 0.2368 g. was dissolved in 9.1 cc. of water; 1 cc. of this solution gave: (i) 8.9, (ii) 9.1, (iii) 9.0 cc. N_2 at 30° and 760 mm. Found N = 37.41; calc. for CH_6N_3OCl; N = 37.67.

(*b*) Using alkali after washing down excess of chlorine, 0.6722 g. dissolved in 30.75 cc. of water; 1 cc. of this solution gave: (i) 5.1, (ii) 5.0, (iii) 5.2 (iv) 5.1 cc. N_2 at 33° and 760 mm. Found N = 24.91; calc. for $^{2}/_{3}$ N_2 = 25.11.

II. With potassium bromate and hydrochloric acid.

(*a*) Using alkali in the presence of bromine, 0.1907 g. was dissolved in 9.6 cc. of water; 1 cc. gave: (i) 7.00, (ii) 6.8, (iii) 6.9 cc. N_2 at 30° and 760 mm. Found N = 37.57; calc. for CH_6N_3OCl; N = 37.67.

(*b*) Using alkali after washing down excess of bromine, 0.6722 dissolved in 30.75 cc. of water; 1 cc. of this solution gave: (i) 5.6, (ii) 5.6, (iii) 5.6 cc. N_2 at 33° and 760 mm. Found N = 27.35; calc. for $^{3}/_{4}$ N_2 = 28.25.

III. With potassium iodate solution.

0.1680 g. dissolved in 9.65 cc. of water; 1 cc. of this solution gave: (i) 4.5, (ii) 4.6, (iii) 4.55 N_2 at 32° and 760 mm. Found N = 28.07; calc. for $^{3}/_{4}$ N_2 = 28.25.

IV. Bromine water.

0.1680 dissolved in 9.6 cc. of water; 1 cc. of this solution gave: (i) 4.5, (ii) 4.45, (iii) 4.6 N_2 at 32° and 760 mm. Found N = 27.89; calc. for $^{3}/_{4}$ N_2 = 28.25.

I am at present engaged in studying the behavior of thiosemicarbazide and carbohydrazide towards the above reagents, and the possibility of estimating chloric, bromic and iodic acids by means of semicarbazide.

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INDIRECT FORMATION OF DOUBLE SALTS.[1] V. THE DOUBLE PLATINIC, CUPRIC AND SILVER IODIDES OF SUBSTITUTED AMMONIUM BASES.

BY RASIK LAL DATTA AND TARAPADA GHOSH

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In continuation of the researches on the indirect formation of double salts, it was thought desirable to test the further applicability of the indirect method used in the preparations of the double salts already described. It was found that this method was applicable not only to the formation of double salts which cannot be obtained by direct means, but also to the preparation of other salts which can be obtained by the direct method, *viz.*, the solution of the insoluble metallic component in the other soluble constituent and crystallization of the double salt from the solution. The preparation of double cupric iodides is not possible directly, since cupric iodide is not stable by itself and decomposes into cuprous iodide and iodine as soon as it is precipitated, or rather, liberated in chemical reactions. It is only when the indirect method is applied that the salt formation is successful. This, as has been pointed out before, is due to the fact that, when the cupric iodide is liberated in the presence of a large excess of ammonium iodide, it at once combines to form the double salt before it has time to decompose into its constituents. This behavior brings the conception of nascent molecules into prominence. The same reason applies to the formation of double carbonates of the alkaline earth metals and lead with potassium carbonate. These could not be prepared by the direct method, *viz.*, the solution of the carbonates of the alkaline earth metals and lead in potassium carbonate. For the preparation of these double salts, the indirect method was employed. This consisted in the precipitation of the carbonates of the alkaline earth metals and lead in the presence of a large excess of a strong solution of potassium carbonate; so that reaction took place between substances in the nascent state, and hence proceeded more readily. In addition to serving for the preparation of double salts, not obtainable by direct means, the indirect method may also be used for the preparation of double salts which can also be prepared by the direct method. This applies to the preparation of double platinic iodides of the substituted ammonium bases which have been prepared by precipitating solutions of the ammonium iodides by chloroplatinic acid. The preparation of double mercuric iodides is a parallel case. Several double mercuric iodides were prepared by the direct method, *viz.*, solution of mercuric iodide in solutions of the alkylamine iodides and crystallization of the double iodide from the resulting solution. The indirect method, however, has done away with the preparation of mercuric iodide at the outset, a solution of mercuric salt added to an excess of substituted ammonium iodide serves for the production of the double salt. In cases of preparation of double salts of other types, however, where an excess of mercuric iodide solution has to be ensured, a solution of mercuric iodide in the potassium iodide has been conveniently used. Similarly, several double cadmium iodides have been prepared by the indirect method.

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[1] Previous communications on the subject:

I. "The Double Platinic and Cupric Iodides of Substituted Ammonium Bases," Datta, *J. Chem. Soc.*, 103, 426 (1913).

II. "Double Carbonates of the Alkaline Earth Metals and Lead with Potassium Carbonate," Datta and Mukherjea, *Proc. Chem. Soc.*, 29, 185 (1913).

III. "The Double Cadmic and Mercuric Iodides of Substituted Ammonium Bases," Datta, THIS JOURNAL, 35, 949 (1913).

IV. "Iodoplatinates of Substituted Ammonium and Sulfonium Bases," Datta, THIS JOURNAL, 35, 1185 (1913).

It is necessary to point out that indirect salt formation fails with the substituted ammonium bases with radicals of low molecular weight, owing to the extreme solubility of the double salts. Nevertheless, the method is susceptible of wide application, being applicable to the formation of double salts generally. The preparation of other double iodides of the series has been undertaken to test the further applicability of the method.

Experimental.

The Double Platinic Iodides (*Iodoplatinates*).—Several of the double platinic iodides of substituted ammonium and sulfonium bases have been described before.[1] It was thought possible that further study might reveal additional points of interest. As is evident, from the former researches, platinic iodide forms double salts of the type $2NR_4I.PtI_4$ only with the alkali metals and the ammonium and sulfonium bases. With, however, piperidinium and coniinium iodides, double salts of the type $4NR_4I.PtI_4$ have been prepared; with guanidinium iodide, a salt of the type $3NR_4I.PtI_4$ and with quinoline ethyliodide and quinaldine ethyliodide salts of the type NR_4I,PtI_4 have been obtained. Furthermore, several double iodides of the series are liquid, which is of considerable interest as affording examples of liquid double platinic iodides.

Piperidinium Platinic Iodide, $4C_5H_{11}NHI.PtI_4$.—On adding a solution of chloroplatinic acid to a strong solution of piperidine hydriodide, a black, shining, crystalline precipitate is formed. This is washed with a small quantity of water and dried in the desiccator. The salt is soluble in water to a beautiful red solution.

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[1] Datta, *J. Chem. Soc.*, 103, 426 (1913); THIS JOURNAL, 35, 1185 (1913).

0.2031 g. gave 0.0262 g. Pt; calc. for $4C_6H_{10}NH_2I.PtI_4$; Pt = 13.12; found, 12.91.

Coniinium Platinic Iodide, $4C_8H_{17}NHI.PtI_4$.—As piperidine forms a salt of the type $4NR_4I.PtI_4$ it was to be anticipated that coniine, which is α-propylpiperidine, would also form a salt of the same type. This has been found to be the case. The double iodide separates as a viscous, dark brown oil on adding chloroplatinic acid to a strong solution of coniinium iodide. This is repeatedly washed by decantation with water and dried as usual in the desiccator.

0.2115 gave 0 0233 Pt; calc. for $4C_8H_{17}NHI.PtI_4$; Pt = 11.23; found 11.03.

Isoquinolinium Platinic Iodide, $2C_9H_7NHI.PtI_4$.—Isoquinoline hydriodide, prepared by neutralizing isoquinoline with hydriodic acid, gave on evaporation a yellowish crystalline powder which on keeping in a desiccator turns reddish violet. The freshly prepared salt is dissolved in water and to it a 10% solution of chloroplatinic acid is added. A black precipitate is obtained which is very sparingly soluble in water, forming a faint yellow solution. It is filtered and, after being washed repeatedly with water, dried in the desiccator. The salt consists of a dark chocolate colored powder.

0.2513 gave 0.0407 Pt; calc. for $2C_9H_7NHI.PtI_4$; Pt = 16.02; found 16.21.

Guanidinium Platinic Iodide, $3CH_5N_3HI.PtI_4$.—Guanidine hydriodide is prepared by neutralizing guanidine carbonate with hydriodic acid and evaporating on the water bath. The double iodide is obtained as a fine, black crystalline precipitate, the solution at the same time turning intensely red. The salt is dried as usual and analyzed.

0.2815 gave 0.0438 Pt; calc. for $3CH_5N_3HI.PtI_4$; Pt = 15.43; found 15 53

Quinoline Ethyl Platinic Iodide, $C_9H_6(C_2H_5)NHI.PtI_4$.—This is obtained as a greenish black precipitate by adding chloroplatinic acid to a solution of quinoline ethyliodide. The salt is very sparingly soluble in water. The filtrate from the precipitate is colored dull yellowish green.

0.2115 gave 0.0417 Pt; calc for $C_{11}H_{11}NHI.PtI_4$; Pt = 19.95; found 19.72.

Quinaldine Ethyl Platinic Iodide, $C_{10}H_9N.C_2H_5I.PtI_4$. – Quinaldine ethyl iodide is only sparingly soluble in water. To a saturated solution of this salt, chloroplatinic acid is added. A momentary light brown precipitate is formed which changes at once to a dirty black-brown. The filtrate has a very faint green color with a faint red fluorescence, and after a day's staying it deposits a further quantity of the precipitate and turns colorless. The salt is highly insoluble in water.

0.3021 gave 0.0591 Pt; calc. for $C_{10}H_9N, C_2H_5I.PtI_4$; Pt = 19.46; found 19.61.

Methylethylpropylphenylammonium Platinic Iodide, $N(CH_3)(C_2H_5)(C_3H_7)(C_6H_5)I.PtI_4$.—This is obtained as a black-brown precipitate by the usual method. The salt is very sparingly soluble in water, the filtrate from the precipitated salt having a very faint green color with a red fluorescence.

The filtrate, on standing, like the preceding salt deposits a further quantity of the precipitate, the solution turning colorless.

0.2631 gave 0.0514 Pt; calc. for $C_{12}H_{20}NI.PtI_4$; Pt = 19.34; found 19.55.

The Double Cupric Iodides.

In addition to the double cupric iodides which have already been described,[1] the following have been prepared by precisely the same method: They are interesting on account of the fact that some of them represent new types and that some of them are liquid at the ordinary temperatures.

Tripropylammonium Cupric Iodide, $3N(C_3H_7)_3HI.2CuI_2$.—A saturated solution of cupric chloride is added to tripropylammonium iodide, when a dark brown oil is precipitated which sinks under water. This is not decomposed by water as was observed previously with some of the higher members. It is washed by stirring with repeated quantities of water in a basin and pouring off the wash water. Finally, the oil is allowed to dry in the desiccator. The compound consists of a dark brown viscous oil.

0.1798 gave 0.0184 CuO; calc. for $3N(C_3H_7)_3HI2.CuI_2$; Cu = 8.67; found 8.16

Trimethyl-p-tolylammonium Cupric Iodide, $N(CH_3)_3C_7H_7I.CuI_2$.—To a saturated solution of trimethyl-*p*-tolylammonium iodide, a saturated solution of cupric chloride is added, when a brick-red precipitate falls down. This precipitate is unaltered by large quantities of water and hence could be washed freely. It is dried in the desiccator.

0.2631 gave 0.0337 CuO; calc. for $N(CH_3)_3C_7H_7I.CuI_2$; Cu = 10.60; found 10.23

Isoquinolinium Cupric Iodide, $2C_9H_7NHI.CuI_2$.—When a saturated solution of cupric chloride is added to a saturated solution of isoquinoline hydriodide, a dark pasty substance is first precipitated which gradually solidifies on stirring with a glass rod. The solidified substance is finally broken up in a mortar and sucked to free it from the adhering mother liquor, when it is obtained as a brown crystalline powder.

0.4364 gave 0.0382 CuO; calc. for $2C_9H_7NHI.CuI_2$; Cu = 7.58; found 6.98.

Triethylsulfonium Cupric Iodide, $2S(C_2H_5)_3I.CuI_2$.—When a saturated solution of cupric chloride is added to a saturated solution of triethylsulfonium iodide, a red-brown oil is precipitated, which appears black in thick layers. The oil is not washed with water since it appears to be decomposed, giving a dirty brown emulsion.

0.2544 gave 0.0230 CuO; calc. for $2S(C_2H_5)_3I.CuI_2$; Cu = 7.78; found Cu 7.22.

Hence cupric iodide forms, altogether, three types of salt, *viz.*, $2NH_4I.CuI_2$, $3NR_4I.2CuI_2$ and $NR_4I.CuI_2$. Of these the first is generally produced and the second and third types are formed only in exceptional cases.

The Double Silver Iodides.

In continuation of the researches on the indirect formation of double salts, the preparation of double silver iodides was undertaken. It is necessary to point out that by the direct method, *viz.*, the solution of silver iodide in solutions of the alkali, ammonia and pyridine hydriodides, corresponding double salts were obtained by other investigators. The only instance of a double silver iodide prepared by the indirect method is tetraethylammonium silver iodide, $N(C_2H_5)_4I.2AgI$ by Stromholm.[1] He prepared the salt by adding silver nitrate to a solution of tetraethylammonium iodide.

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[1] *Loc. cit.*

It is interesting to note that the formation of the double salts of silver by the indirect method only holds with the substituted ammonium bases of high molecular weight. With the low molecular weight substituted ammonium bases, the formation of double salts does not take place, pure silver iodide being the precipitate on the addition of silver nitrate to the ammonium iodide solutions. This is due to the small affinity between silver iodide and the alkali and ammonium iodides. It is for this reason that those double iodides of silver with the alkali metals and ammonia which can be prepared by the direct method, are at once decomposed into the constituents when treated with water. It is to be noted that two series of salts have been obtained; with tetramethylammonium iodide, as well as with pyridine or quinoline hydriodide, salts of the type $NR_4I.2AgI$ are formed; but with tetrapropylammonium iodide, a salt of the type $2N(C_3H_7)_4I.3AgI$ is formed.

The following double iodides have been prepared by adding a solution of silver nitrate to a saturated solution of the substituted ammonium iodides.

Tetramethylammonium Silver Iodide, $N(CH_3)_4I.2AgI$.- To a strong solution of tetramethylammonium iodide a strong solution of silver nitrate is added, with constant shaking and stirring. A white precipitate, with a faint yellow tinge is obtained. This is filtered and dried in the steam chamber.

0.2271 gave 0 1553 AgI, calc for $N(CH_3)_4I$ 2AgI, Ag = 32.19, found 31 44

This and other salts of the series are decomposed by boiling with dilute nitric acid, leaving pure silver iodide.

Trimethyl-p-tolylammonium Silver Iodide, $N(CH_3)_3C_7H_7I.2AgI$.—This is obtained as a white precipitate by adding a solution of silver nitrate to a moderately strong solution of trimethyl-*p*-tolylammonium iodide. The precipitate is washed with water and dried in the steam chamber.

Pyridinium Silver Iodide, $C_5H_5NHI.2AgI$.—This is obtained as a white precipitate by the usual method described above. It is dried in the steam chamber.

0.3005 gave 0.2057 AgI; calc. for $C_5H_5NHI.2AgI$; Ag = 31.70; found 31.39.

Quinolinium Silver Iodide, $C_9H_7NHI.2AgI$.—This is obtained as a white precipitate which is washed, and dried in the steam chamber.

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[1] *Ber.*, **36**, 142 (1903).

0.2931 gave 0.1849 AgI; calc. for $C_9H_7NHI.2AgI$, Ag = 29.51; found 28.99.

Tetrapropylammonium Silver Iodide, $2N(C_3H_7)_4I.3AgI$.—With tetrapropylammonium iodide, quite a distinct type of salt is obtained, *viz.*, $2NR_4I.3AgI$, whereas in the case of other salts, the type $NR_4I.2AgI$ is produced. The latter type is the one usually formed whereas the former type is only exceptional, being obtained mainly with the heavy bases. The salt is obtained as a white precipitate by adding a solution of silver nitrate to tetrapropylammonium iodide. The precipitate is washed and dried at 100°.

0.2533 gave 0.1324 AgI; calc. for $2N(C_3H_7)_4I.3AgI$; Ag = 24.32; found 24.02.

Investigations on similar lines are being continued.

CHEMICAL LABORATORY, PRESIDENCY COLLEGE,
CALCUTTA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A STUDY OF THE MECHANISM OF THE GRIGNARD REACTION.

BY LAMBERT THORP AND OLIVER KAMM

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Introduction.

Ever since the time when Grignard pointed out that the reaction between magnesium and alkyl or aryl halides was much facilitated if the latter were dissolved in ether, various opinions have, from time to time, been promulgated concerning the role of the solvent in the reaction. Evidence appears to be at hand pointing to the conclusion that the ether forms one or more definite compounds with the magnesium alkyl (or aryl) halide. Thus, in the case of methyl iodide, Grignard observed that an addition product of the formula $(C_2H_5)_2O.MgCH_3I$ was left, after the excess of ether had been removed in a vacuum. Grignard at first held the view that this molecule of ether functioned as ether of crystallization. Further evidence regarding the existence of definite compounds of ether and magnesium alkyl halides has been furnished by Tschelinzeff,[1] who showed that the addition of ether to a benzene solution of magnesium alkyl halide caused the evolution of definite and equal amounts of heat for each of the first two molecular quantities of ether added. Such an addition product would thus correspond to Zelinsky's compound $2(C_2H_5)_2O.MgI_2$.

A definite idea regarding the distribution of valences in the ether addition products was first put forward by Baeyer and Villiger,[2] who, with the work of Collie and Tickle[3] in mind, believed that they had in this class of compounds further evidence to strengthen their belief in the existence of tetravalent oxygen. Three years previously Collie and

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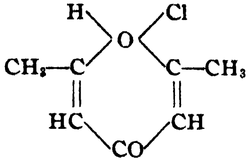
[1] *Ber.*, 37, 2084 (1904); *Ibid.*, 37, 4534 (1904); *Ibid.*, 39, 773 (1906).

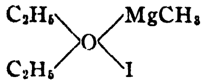
[2] *Ibid.*, 35, 1201 (1902).

[3] *J. Chem. Soc.*, 75, 710 (1899).

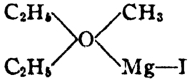
Tickle[1] had found that dimethyl pyrone formed a well defined addition product with hydrogen chloride to which they assigned an oxonium structure:



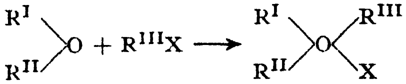
Accordingly, Baeyer and Villiger represented the substance $(C_2H_5)_2O.$-$MgCH_3I$ by a somewhat analogous oxonium arrangement:



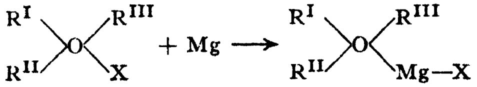
Grignard himself finally adopted an oxonium structure, but distributed the four valences of the oxygen in a different manner:



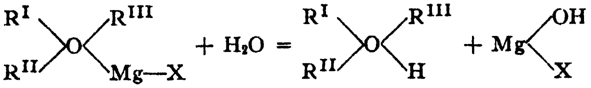
Recently, G. Stadnikoff[2] has undertaken to defend the view of Grignard regarding the oxonium structure of the addition products of ethers and magnesium alkyl halides. His theory concerning the mechanism of the reaction involves first the formation of an oxonium compound through the reaction between the ether and the alkyl halide:



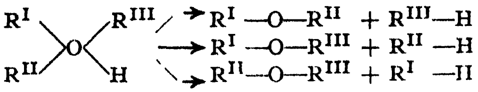
This product is then acted upon by the magnesium to form a monoetherate:



Upon treatment with water this latter compound is decomposed in the sense of the following requation to give another oxonium derivative:



Being very unstable this substance may break up in several directions:



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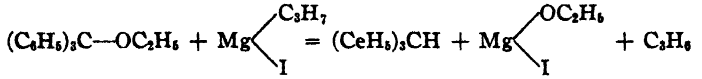
[1] *Loc. cit.*

[2] *J. Russ. Phys. Chem. Soc.*, **43**, 1244 (1911); *C. A.*, **6**, 1434 (1912); *J. Russ. Phys. Chem. Soc.*, **44**, 1219, 1256 (1912); *C. A.*, **7**, 983, 984 (1913); *Centr.*, **1**, 21, 22 (1913); *J. Russ. Phys. Chem. Soc.*, **44**, 1247 (1912); *Ber.*, **44**, 1157 (1911); *Ibid.*, **46**, 2496 (1913); *J. prakt. Chem.*, [2] **88**, 1 (1913).

What lends apparent strength to the hypothesis of Stadnikoff, is this very multiplicity of products, as a concrete example of which might be cited the following case: Upon decomposing, by means of dilute sulfuric acid, the reaction product from magnesium, propyl iodide and diphenylmethyl butyl ether, he obtained symmetrical tetraphenyl ethane, 1,1-diphenyl-butane, hydrogen, and diphenylmethyl propyl ether.

A. I. Gorski,[1] in his criticism of the work of Stadnikoff, has pointed out the possibility of interpreting his results on the basis of hydrolysis and reduction, or of direct reduction, of the ethers from analogy to the behavior of zinc alkyls:

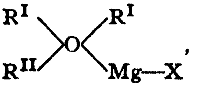


$$(C_6H_5)_3C{-}OC_2H_5 + Mg\begin{matrix}\diagup C_3H_7\\ \diagdown I\end{matrix} = (CeH_5)_3CH + Mg\begin{matrix}\diagup OC_2H_5\\ \diagdown I\end{matrix} + C_3H_6$$

His argument is further strengthened by a consideration of the results of his work upon the behavior of organo-magnesium compounds towards other oxygenated substances.

Theoretical.

Upon the basis of the conception of Stadnikoff, regarding the constitution of the addition products resulting from the action of ethers upon organo-magnesium compounds, it should be possible to arrive at any given oxonium structure by employing two different combinations of ether and halogen derivative; that is to say, for example, it should be possible to generate the oxonium compound,



$$\begin{matrix}R^I\\R^{II}\end{matrix}\!\!>O<\!\!\begin{matrix}R^I\\Mg{-}X\end{matrix},$$

from the two combinations: (1) $R^I{-}O{-}R^I.R^{II}X$ and (2) $R^I{-}O{-}R^{II}.$-R^IX. The evidence as to whether or not identical addition products had been formed in the two cases could be furnished by a consideration of the nature of the decomposition products. Thus, upon treatment with dilute acids and carbon dioxide, respectively, the hydrocarbons, $R^I{-}H$ and $R^{II}{-}H$, and the acids $R^I{-}COOH$ and $R^{II}{-}COOH$ should not only be generated in both cases, but their ratios should be equal. It is the object of the present work to test this deduction from Stadnikoff's oxonium hypothesis by employing first, the combination, diethyl ether and phenyl bromide, and second, phenetole and ethyl bromide.[2]

Upon decomposing, by means of dilute sulfuric acid, the product resulting from the reaction of magnesium upon a mixture of diethyl ether and bromobenzene, a yield of benzene amounting to 61% of the theoretical was obtained, as well as a considerable quantity of diphenyl and a small volume of gas. This gas, upon examination, proved to be a mixture of ether vapor, hydrogen, air, a hydrocarbon (or hydrocarbons) insoluble in fuming sulfuric acid, and possibly some ethylene. Upon treatment of an ethereal solution of phenyl magnesium bromide with carbon dioxide, the sole product was benzoic acid, whereas the hypothesis demands the simultaneous formation of propionic acid.

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[1] *J. Russ. Phys Chem Soc*, **44**, 581 (1912); *Chem. Centr.*, **2**, 1527 (1912); *J. Russ. Phys. Chem. Soc*, **45**, 163 (1913); *J. Chem. Soc.*, **104**, 1, 462 (1913).

[2] It is here assumed that the excess of ether used as a solvent does not change the nature of the decomposition products. It is our purpose to investigate the influence of this factor

In the case of the combination, phenetole, ethyl bromide and magnesium, the decomposition products with dilute sulfuric acid and carbon dioxide were ethane and propionic acid, respectively. Neither benzene nor benzoic acid could be detected. The yield of ethane, based upon the magnesium in solution, was 97% of the theoretical, whereas in the case of bromobenzene and diethyl ether the yield was less than 0.2%.

Experimental.

Diethyl Ether, Bromobenzene and Magnesium.

Decomposition with Dilute Sulfuric Acid.—The solution of phenyl magnesium bromide was prepared in the usual manner from 12.2 g. (0.5 mol) of magnesium ribbon, 79 g. (0.5 mol) of bromobenzene and 100 g. of anhydrous ether. At the end of 2.5 hours 0.3 g. of magnesium remained undissolved; and the solution was made up to 250 cc. by the addition of a sufficient amount of anhydrous ether.

Three cubic centimeters of the above solution were introduced into a buret filled with 70% sulfuric acid at a temperature of 50°. The ether was readily absorbed, a layer of benzene separated on the surface of the acid, and approximately 1 cc. of gaseous product was obtained.

In order to examine the latter, 100 cc. of the original solution were decomposed in the same way. The resulting gas measured 27.55 cc., which, after treatment with fuming sulfuric acid, decreased to 21.45 cc. An alkaline pyrogallol solution reduced this volume to 21.10 cc. After the addition of 18.8 cc. of oxygen to 11.2 cc. of the residual gas, and explosion of the mixture, the volume of gaseous product was 15.5 cc. After treatment with a solution of caustic potash the resulting gas measured 12.10 cc., and the contraction, 3.4 cc., represents the volume of carbon dioxide. If we assume the hydrocarbon present to be ethane, the data indicate that only 1.7 cc. were formed from the decomposition of approximately one-tenth of a mol of the Grignard solution, while the amount of hydrogen was 6.8 cc. The benzene was found to be soluble in fuming sulfuric acid without leaving any residual gas.

The benzene obtained from a second 100 cc. portion of phenyl magnesium bromide solution was dried over calcium chloride, purified by shaking with concentrated sulfuric acid, and distilled. Nine grams (b. p. 78–82°) were obtained. The residue in the distilling bulb yielded upon distillation 1 g. of pure diphenyl. The above weight of benzene, based upon the bromobenzene, and corrected for the amount of diphenyl formed, corresponds to 61% of the theoretical.

Decomposition with Carbon Dioxide.—A current of dry carbon dioxide was passed for 3 hours into 50 cc. (0.1 mol) of the cool Grignard solution prepared above. At the end of this time the viscous mass was decomposed by means of dilute sulfuric acid, and then extracted with ether six times, the total volume of ether extract amounting to 350 cc. Since hydrobromic acid could not be detected in this extract, it was possible to determine the total acidity, due to organic acids, by direct titration after evaporation of the ether. Ten cubic centimeters of the ether solution required 29.00 cc. $Ba(OH)_2$ (0.0281 *N*).

A second (50 cc.) portion of the ether extract was evaporated on the water bath, and the acid taken up with 100 cc. of hot water. The solution was allowed to cool to room temperature (22°), and the excess of benzoic acid filtered off. The filtrate, a saturated solution of benzoic acid, and suspected to contain some propionic acid, was subjected to distillation. An equal volume of a solution of benzoic acid, saturated under the same conditions was distilled at the same time. The results are tabulated below, column A containing the values for the acid solution resulting from the decomposition of the Grignard compound, and column B the values for the blank saturated solution of benzoic acid.

	(0.0281 *N*). Cc. $Ba(OH)_2$. A.	(0.0281 *N*). Cc. $Ba(OH)_2$. B.
1st 10 cc. distillate	1.60	1.72
2nd 10 cc. distillate	1.95	2.05
3rd 10 cc. distillate	2.10	2.05
4th 10 cc. distillate	2.32	2.25
5th 10 cc. distillate	2.55	2.55

Ten cubic centimeters of the saturated benzoic acid solution were found to be equivalent to 7.95 cc. $Ba(OH)_2$ solution. A comparison of the above values for benzoic acid with the Duclaux constants for propionic acid indicates that the latter acid distils in a current of steam five times as rapidly as benzoic acid, and we should, therefore, expect a large per cent. of the propionic acid to be found in the first portions of the distillate. Calculations show that the above method, allowing an error of 0.1 cc. in the values for the $Ba(OH)_2$ titrations, is capable of detecting as little as 0.0015 g. of propionic acid in 100 cc. of solution. The close agreement obtained between the values for the two solutions indicates that propionic acid was absent. The yield of benzoic acid obtained amounted approximately to 50% of the theoretical.

Phenetole, Ethyl Bromide and Magnesium.

Decomposition with Dilute Sulfuric Acid.—A mixture of 60 g. of phenetole, 2.4 g. of magnesium in the form of ribbon, 12 g. of ethyl bromide and a crystal of iodine was warmed until solution of the greater part of the magnesium had been effected. The reaction was considerably more sluggish than in the former case. Butane was evolved, and a precipitate of magnesium iodide separated.

Three cubic centimeters of the clear solution were introduced into a buret filled with 5% sulfuric acid, and the resulting gas was drawn off by means of a mercury attachment and examined as described below. After purification by treatment with fuming sulfuric acid, the volume of gas was 35.9 cc. (13° and 727.5 mm.). The results of the explosion with an excess of oxygen indicate that the gas was pure ethane: 5.1 cc. gas produced 10 cc. CO_2, 4.9 cc. gas produced 10.1 cc. CO_2. In the dilute sulfuric acid which had been used for the decomposition of the phenetole solution the magnesium was determined as pyrophosphate. Wt. $Mg_2P_2O_7$ = 0.2004 g. The agreement between the volume of ethane, predicted upon the assumption that 22.4 liters of the gas are equivalent to 24.3 g. of magnesium, and the volume actually found, is shown in the following table:

	Cc.
Volume ethane (0 : 760 mm.)	32.8
Volume ethane (0 : 760 mm) soluble in 3 cc. phenetole	7.4
Total volume ethane	40.2
Volume ethane equivalent to 0.2004 g. $Mg_2P_2O_7$	40.3

The yield of ethane is evidently about 99.7% of the theoretical. Assuming a maximum error of 1 cc. in the several determinations, the yield of ethane is still more than 97%.

Decomposition with Carbon Dioxide.—A current of dry carbon dioxide was passed into 50 cc. of the cool phenetole solution, prepared in the preceding experiment. After about two hours, ice water was added to the viscous mass, and then enough ammonium chloride to dissolve the magnesium hydroxide. After separation of the phenetole the aqueous layer was acidified with dilute sulfuric acid, and one-half of the solution (110 cc.) was distilled according to the method of Duclaux. The results were as follows:

1st 10 cc. distillate required 8.60 cc. KOH (0.115 *N*)
2nd 10 cc. distillate required 8.65 cc. KOH (0.115 *N*)
3rd 10 cc. distillate required 6.85 cc. KOH (0.115 *N*)
4th 10 cc. distillate required 5.98 cc. KOH (0.115 *N*)

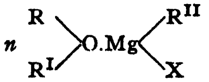
Not a trace of halogen acid could be detected in any portion of the distillate before the fifth.

In order to test for benzoic acid the second half of the solution was made strongly alkaline with potassium hydroxide, evaporated on the water bath to small bulk, cooled, acidified with dilute sulfuric acid, and extracted repeatedly with ether. The ether was distilled, and the residue taken up with 30 cc. of hot water. Upon cooling, no benzoic acid separated out.

For the purpose of detecting minute traces of benzoic acid, an aqueous solution of copper propionate was employed. Preliminary tests had shown that this reagent was capable of giving a distinct precipitate in a neutral solution of benzoic acid at a dilution of 1 : 10,000. Since no precipitate was formed in the 30 cc. portion of neutral solution, benzoic acid, if produced at all in the reaction, must have been present in an amount less than 0.006 g.

Conclusions.

1. The action of an alkyl (or aryl) halide upon magnesium in the presence of an ether results in the formation of certain addition products which may be represented by the general formula



$$n\,\frac{R}{R^{I}}>O.Mg<\frac{R^{II}}{X}$$

2. The Grignard-Stadnikoff oxonium structure predicts that a given etherate may be prepared by either of two methods. Experimental data, however, indicate that the compounds formed are not identical—in fact all the evidence obtained is contrary to the theory of Stadnikoff.

3. It is unnecessary to assume any oxonium structure for the Grignard compounds in order to account for the decomposition products obtained with the common ethers (diethyl and phenyl-ethyl). If, however, the assumption of an oxonium structure is desired, the Baeyer-Villiger formula is to be preferred.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SOME TRANSFORMATIONS OF RICINOLEIC AND OLEIC ACIDS.

[SECOND PAPER.]

ACTION OF MONOPOTASSIUM ANILIDE AND POTASSIUM PHENOLATE UPON DIBROMOHYDROXYSTEARIC AND DIBROMOSTEARIC ACID.

BY B. R HONOVSKI

Received March 5, 1914

In my previous paper[1] it was shown that ricinoleic acid was changed to diiodostearic by the action of hydriodic acid. This acid upon reduction with nascent hydrogen is changed quantitatively to stearic acid. This reaction makes it certain that the iodine atoms in diiodostearic acid are not added to two neighboring carbon atoms:

$$CH_3(CH_2)_5CHI—CH_2—CHI—CH_2(CH_2)_7COOH,$$

$$CH_3(CH_2)_5CHI—CH_2—CH_2—CHI(CH_2)_7COOH,$$

otherwise, upon reduction with nascent hydrogen, an unsaturated acid would be obtained, similar to the dihalogen oleic, elaidic, fumaric, and maleic acids, which, upon reduction of their respective dihalogen-derivatives, give the original acids or their isomers. Consequently the formula:

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[1] *Ber.*, 42, 3339 (1909).

$$CH_3(CH_2)_6CHOH—CH=CH—(CH_2)_7COOH,$$

which has been proposed by Kraft[1] and based upon decomposition products of ricinoleic acid, cannot be accepted. An acid having hydroxyl and a double bond situated at two neighboring carbon atoms, should, upon action of HI, yield also a diiodo acid with neighboring iodine atoms and this would give an unsaturated acid upon reduction with nascent hydrogen.

The property which ricinoleic acid has of passing into stearic and dihydroxystearic acid with hydroxyl groups situated at two carbon atoms not adjacent, and into ricinstearolic acid, $CH_3(CH_2)_5—CHOH—CH_2—C\equiv C—(CH_2)_7COOH$, which formula was given by Goldsobel,[2] and, on the other hand, the products of decomposition of ricinoleic acid such as oenanthol and undecylic acid obtained by destructive distillation or by oxidation with nitric acid[3] point to the fact that the constitution of ricinoleic acid may be expressed by the formula:

$$CH_3(CH_2)_5CHOH-CH_2—CH=CH—(CH_2)_7COOH$$

Desiring to obtain some data which would throw more light on this subject, and at the same time wishing to investigate the action of monosubstituted anilide and phenolate upon dihalogen hydroxy and dihalogen fatty acids, the following experiments were undertaken.

It was desired to obtain in the first case dianilidoderivatives of ricinoleic and oleic acid:

$$CH_3(CH_2)_5CHOH\quad CH_2-CH(NHC_6H_5)-CH(NHC_6H_5)—(CH_2)_7COOH$$

and

$$CH_3(CH_2)_7-CH(NHC_6H_5)-CH(NHC_6H_5)-(CH_2)_7COOH,$$

or, if such compounds are not capable of existence, certain definite products of their decomposition.

Experimental.

Dibromohydroxystearic acid.—This acid was prepared in the usual way by adding 55 g. of Br to 100 g. of ricinoleic acid. After all of the acetic acid and ether were gone, a small amount of benzene (25–30 cc.) was added to dibromohydroxystearic acid and mixed thoroughly with 50 g. of dry and finely pulverized potassium carbonate. The mixture was kept on the water bath for a few hours, with occasional stirring and addition of benzene to prevent the product from passing into a solid mass.

For 150 g. of dibromohydroxystearic acid, 180 g. of monopotassium anilide were added (double the theoretical amount). This was prepared by gradually adding 52 g. of potassium to 200 g. of aniline, diluted with benzene to keep the product in liquid form.

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[1] *Ber.*, **21**, 2730 (1888).

[2] *Ibid.*, **27**, 3121 (1894).

[3] *Ann.*, **120**, 288 (1861); *Ber.*, **23**, [2] 444 (1890); **24**, 979 (1891).

The reaction between potassium and aniline takes place at the ordinary temperature, but after a while it is necessary to heat the mixture on the water bath and stir occasionally to distribute the melted potassium throughout the viscous liquid until all is dissolved.

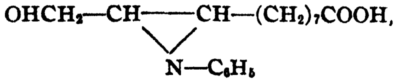
The casserol containing potassium anilide was placed in ice water and the potassium salt of dibromohydroxystearic acid was added in small portions and mixed thoroughly. After standing for 2–3 hours at ordinary temperature, the mixture was kept on the water bath for 12–15 hours with frequent stirring, and after all of the benzene was gone the product was placed in a porcelain dish, water was added and the mixture was brought to boiling. While still hot, the product was decomposed by adding hydrochloric acid and boiling for half an hour. The tarry oil, which solidifies on cooling, was removed from the surface and dissolved in ligroin. The solution was kept on the water bath and stirred with a glass rod to help the separation of the tarry matter which solidifies on the bottom. The liquid was poured to another beaker, which was kept for a while on the water bath until the ligroin solution became clear. In this way most of the tarry matter was separated. Then the ligroin was distilled off and the product was dissolved in alcohol and boiled with some excess of dry sodium carbonate and filtered very slowly into a solution of barium chloride with constant stirring. After the precipitation was completed, the clear liquid was poured off, if the precipitate sticks to the walls of the dish, or filtered if the precipitate was flocculent, and thoroughly dried. The dry precipitate was placed in a flask and digested with ether for a few days at the ordinary temperature, occasionally shaking. The ether solution was filtered off and digestion was repeated for 1-2 days. The ether was then filtered off and the residue washed on the filter with ether and decomposed by boiling with dilute hydrochloric acid. The fatty product which solidifies on the surface was removed, dried and dissolved in ligroin. After a few crystallizations from ligroin containing a little ether the product was further purified by boiling its alcoholic solution with animal charcoal for 20 hours. For further purification, the alcoholic solution was saturated with dry sodium carbonate and precipitated with barium chloride. The barium salt was recrystallized from boiling water, by adding salt in excess to water (3–4 liters), boiling for one-half hour and filtering hot.

By this method all other fatty acids, such as palmitic, stearic and some derivatives of oleic acid, were separated as insoluble in water. For the above reason the purification of ricinoleic acid by means of the lead salt can be avoided. The bulk of the solid acids can be separated by cooling ricinoleic acid below room temperature and filtering off.

The acid, which was obtained from the barium salt and recrystallized from ligroin and ether, crystallizes in shining leaves, which melt at 57–58°.

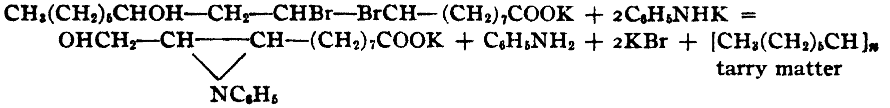
It is soluble in all commonly used solvents and sparingly in hot water. Yield, about 35% theoretical.

Analyses of this substance gave results corresponding to the formula:



$$\underbrace{OHCH_2{-}CH{-}{-}CH}_{N{-}C_6H_5}{-}(CH_2)_7COOH,$$

which shows that one molecule of monopotassium anilide replaces *both* bromine atoms situated at the neighboring carbon atoms. The hydroxyl group of dibromostearic acid is shifted toward the carboxyl group and the molecule of hydroxy dibromostearic acid splits up, giving 11-hydroxy-9,10-anilido undecylic acid,



$$CH_3(CH_2)_5CHOH{-}CH_2{-}CHBr{-}BrCH{-}(CH_2)_7COOK + 2C_6H_5NHK =$$
$$\underbrace{OHCH_2{-}CH{-}{-}CH}_{NC_6H_5}{-}(CH_2)_7COOK + C_6H_5NH_2 + 2KBr + \underbrace{[CH_3(CH_2)_5CH]_n}_{\text{tarry matter}}$$

where both hydrogen atoms of the amino group are replaced, as follows from the reaction with nitrous acid, which has no effect on hydroxyanilidoundecylic acid:

Samples of this acid gave the following results on combustion with copper oxide and copper spiral:

0 2165 and 0.2210 g subs. gave C = 69 83, 69 68; H = 8.85, 8.92; calc. for $C_{17}H_{25}NO_3$, C = 70.10 and H = 8.59

The amount of nitrogen was determined by the Kjeldahl method:

0.3630, 0.4350 g.; N, 4.54, 4.41; calc for $C_{17}H_{25}NO_3$, N = 4.81

The barium and silver salt were prepared by saturating an alcoholic solution of the acid with dry sodium carbonate and precipitating the filtrate with barium chloride and silver nitrate.

Both salts are soluble in water and alcohol.

0.3290 g. of the Ba salt gave 18 76% Ba and 0 4130 g gave 19.09% Ba; calc. 19.10% Ba.

0.6810 g. Ag salt gave 27 01% Ag, and 0.3085 Ag salt gave 26 90% Ag; calc. 27 13% Ag.

Acetic Ester of Hydroxyanilido Undecylic acid.—The presence of the hydroxyl group in the acid was proved by obtaining the acetic ester of the acid by heating the acid with ten times the amount of acetic anhydride, required by theory in a sealed tube at 110° during 8 hours.

It is a colorless viscous liquid which saponifies with caustic alkali to the hydroxy acid. The saponification was done in alcoholic solution, using 3–4 times the quantity of metallic sodium necessary to neutralize the products of saponification. The blank sample was run at the same time, using alcohol from the same bottle.

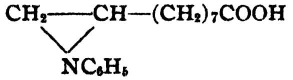
1.1395 of the ester required 0.1568 Na = 13.76% Na.
1.2535 of the ester required 0.1714 Na = 13.67% Na.
Calculated for ($C_2H_3O_2Na + C_{17}H_{24}NO_3Na$) 13.81% Na.

Lactone of Hydroxyanilidoundecylic Acid.—Hydroxyanilidoundecylic acid, on standing for a few weeks, gradually becomes liquid and by loss of one mol of water is converted to the lactone.[1] The same change takes place upon warming the acid with dilute (1–2) H_2SO_4 for a few hours on the water bath. The lactone is easily saponified to the hydroxy acid.

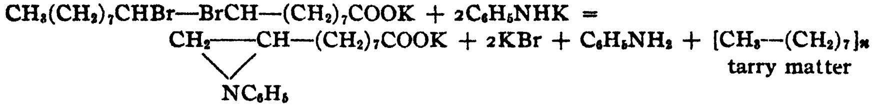
0.2315 and 0.2420 g. lactone gave 74.38 and 74.46% C; and 8.93 and 8.70% H. Calc. for $C_{17}H_{23}NO_2$, C, 74.72; H, 8.42.

Dibromohydroxyanilidoundecylic Acid.—This was prepared in the usual way, using dry ether and glacial acetic acid as a solvent. The amount of bromine was added in the proportion of about three atoms of bromine to one mol of the acid. During bromination and on standing for twelve hours, as well as during evaporation of the solvents on the water bath, no evolution of hydrobromic acid was noticed. The dibromohydroxyanilido acid is a viscous yellow liquid which, after a few months of keeping in the desiccator, decomposes slightly. Upon reduction with zinc dust in glacial acetic acid, the compound was changed to the original acid. This reaction and the ability to combine with bromine without evolution of hydrobromic acid brings us to the conclusion that the reaction with Br is a simple additive one.

0.2965 g. of the bromide gave 35.28 and 0.3120 g. of the bromide gave 35.32% Br Calc. for $C_{17}H_{25}Br_2NO_3$, 35.47% Br.



9-10-Anilidodecylic Acid, $\underset{NC_6H_5}{\underset{\diagdown\diagup}{CH_2\text{——}CH}}\text{—}(CH_2)_7COOH$ was obtained in exactly the same manner as hydroxyanilidoundecylic acid. Dibromostearic acid, which was prepared by adding bromine to oleic acid, was changed to the potassium salt as described above and mixed with double amount of monopotassium anilide.



$$\begin{array}{l} CH_3(CH_2)_7CHBr\text{—}BrCH\text{—}(CH_2)_7COOK + 2C_6H_5NHK = \\ \qquad \underset{NC_6H_5}{\underset{\diagdown\diagup}{CH_2\text{——}CH}}\text{—}(CH_2)_7COOK + 2KBr + C_6H_5NH_2 + \underset{\text{tarry matter}}{[CH_3\text{—}(CH_2)_7]_x} \end{array}$$

The separation of the acid from the tarry matter is carried out in the same order as described above, but the purification of the acid by crystallizing its barium salt from hot water was omitted. 9,10-Anilidodecylic acid is a white amorphous powder, which melts at 54–55°, is soluble in all commonly used solvents, but not in water, and does not combine with bromine.

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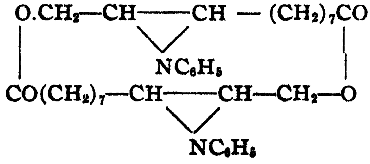
[1] The analysis also corresponds to the formula of the lactide



$$\begin{array}{l} O.CH_2\text{—}\underset{NC_6H_5}{\underset{\diagdown\diagup}{CH\text{——}CH}}\text{—}(CH_2)_7CO \\ | \qquad\qquad\qquad\qquad\qquad | \\ CO(CH_2)_7\text{—}\underset{NC_6H_5}{\underset{\diagdown\diagup}{CH\text{——}CH}}\text{—}CH_2\text{—}O \end{array}$$

Analyses of this acid gave the following data:

0.2030 and 0.1880 g. acid gave C = 73.30 and 73.41; H, 9.07, 8.95. Calc. for $C_{16}H_{22}NO_2$, C = 73.56 and H = 8.81; 0.4020 and 0.4240 g. subs. gave (Kjeldahl method) N = 5.15 and 5.18; calc. N = 5.36.

The barium and silver salts were prepared by precipitating the sodium salt of the acid with $BaCl_2$ and $AgNO_3$ solution. Both salts are insoluble in water.

0.1995 g. of silver salt gave 29.32% Ag; 0.2570 of barium salt gave 20.59% Ba; calc. for $C_{17}H_{22}NO_2Ag$, 29.34% Ag; $(C_{17}H_{22}NO_2)_2$ Ba, 20.85% Ba.

The difference in chemical properties between hydroxyanilidoundecylic acid and anilidodecylic acid is the readiness of the first acid to form a dibromoderivative. The second acid does not combine with bromine.

On applying a 1 or 2% solution of potassium permanganate in order to change the hydroxyanilido acid to the trihydroxy acid, it was found that some decomposition took place, but most of the acid was recovered unchanged. This reaction gives a certain proof, that hydroxyanilidoundecylic acid does not possess a double bond in the open chain, and consequently the two bromine atoms are situated in the benzene ring.

Phenoxy Derivatives of Oleic Acid were obtained by the action of phenol on dibromostearic acid in the presence of potassium carbonate. Dibromostearic acid was mixed with 180 g. of pulverized potassium carbonate and 150 g. of phenol. The mixture was heated for twelve hours at 105 108° and frequently stirred. Then water was added and the product was salted out as a viscous mass and warmed for some time with a solution of barium chloride. The water was poured off and the precipitate of barium salt, a viscous mass, was left on the same dish to dry and then transferred to the flask and boiled for a while with alcohol in order to take up the moisture and some phenol remaining. After cooling the alcohol was poured off and ether was added to extract the oily decomposition products of dibromostearic acid. In this ethereal solution was found also a considerable quantity of unchanged dibromostearic acid.

The barium salt remaining undissolved in ether was decomposed by boiling with dilute hydrochloric acid and the product was removed after cooling and dissolved in ligroin on the water bath. A small part of this product was left undissolved in ligroin and was filtered off. The first part of this product, which was readily soluble in ligroin, was crystallized out of ligroin and alcohol. It is a white crystalline powder with characteristic odor which melts at 58-59° and according to analysis corresponds to the formula:

$$CH_2 - (OC_6H_5) - (CH_2)_7COOH$$

0.1985 g. and 0.2050 g. subs. gave C = 71.63 and 71.56; H = 9 11 and 9.21; calc. for $C_{15}H_{22}O_3$, C = 72.00; H = 8.80.

The barium and silver salts were prepared by precipitation of sodium salt with $BaCl_2$ and $AgNO_3$.

0.4090 g. of the Ag salt gave 30.19% Ag; 0.4670 g. of the Ag salt gave 30.08% Ag; calc. for $C_{15}H_{21}O_3Ag$, Ag = 30.25; 0.3315 and 0.2845 g. of the Ba salt gave 21.50 and 21.42% Ba; calc. for $(C_{15}H_{21}O_3)_2Ba$, Ba = 21.59.

The bromide was prepared by adding two atoms of bromine to one mol of the acid. It is a crystalline monobromosubstituted phenoxyacid.

0.1440 and 0.1275 of the bromide gave 24.18 and 24.09% Br; calc. for $C_{15}H_{21}BrO_3$, Br = 24.31.

Condensation Product.—The second part of this product, obtained in very small quantity (about 1 g.), which is not soluble in ligroin but readily in alcohol, and very readily in acetic acid, is a white crystalline powder which melts at 96–97°.

0.4615 g. of its silver salt gave 11.70% Ag and 0.1790 g of the bromide gave 0.0875 AgBr = 20.79% Br.

Judging from these data, this acid is probably a condensation product of the decomposition products of the phenoxyacids and corresponds to the formula $C_{60}H_{94}O_6$.—$3CH_3(CH_2)_7CH_2(C_6H_5O) + CH_2(C_6H_5O)(CH_2)_7COOH$— for which the calculated amount of silver is 11.88% and of bromine calculated for a tribromosubstituted derivative is 20.87%.

The next experiment for the preparation of phenoxyacids was carried out in the same manner as described above, but the temperature was raised to 140° and kept there during twenty hours. This product crystallizes from alcohol in large aggregates consisting of long needles, m. p. 54–55°. The data obtained by analyzing this acid closely correspond to those of the first acid $CH_2—(C_6H_5O)—(CH_2)_7COOH$ as follows:

0.2005 and 0.2120 g. of the acid gave C = 72.06 and 72.13; H = 8.67 and 8.72; 0.1035 g. of the barium salt gave 21.53% Ba; 0.3160 g. of silver salt gave 0.0955 Ag = 30.22% Ag.

The bromide is a white crystalline substance.

0.1470 and 0.1210 g. of the bromide gave 24.02 and 24.06% Br.

The identity in composition of these two acids established by analyses, and the difference in physical properties points out that the last acid is either isomeric with the first acid or its molecule consists of two molecules of the first acid. Consequently it was necessary to determine the molecular weight of these two acids.

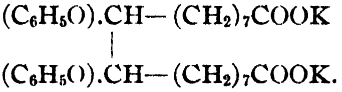
The determination was done by using the Eijkmann cryoscopic apparatus, using as a solvent glacial acetic acid. In spite of care to prevent the solvent from taking up moisture, a few determinations of different concentration of the solutions gave a depression of melting point corresponding to a molecular weight of the first acid $CH_2—(C_6H_5O)—(CH_2)_7$-COOH, 272–279 against 250; and 516–526 against 498 for

$$\begin{array}{l} CH.(C_6H_5O)—(CH_2)_7COOH \\ | \\ CH.(C_6H_5O)—(CH_2)_7COOH \end{array}$$

The increased concentration of the solution gives an increase in molecular weight.

The data obtained differ greatly from those obtained by analyses and the difference between the values of each one of the above acids is too considerable to admit assigning a value to any one of these determinations by themselves. In comparison with each other, however, they show that the molecular weight of the second acid is much greater (almost double the first acid). Taking into consideration that these two acids are formed under different conditions in temperature and were not found together in any proportions in the same experiment and the difference in crystalline form and molecular weight, it will be necessary to admit that the second of these acids is a condensation product of the first and its formula will be according to the formation:

$$CH_3(CH_2)_7CHBr—CHBr(CH_2)_7COOK + 2C_6H_5OK =$$
$$CH_3(CH_2)_7CH(C_6H_5O)—(C_6H_5O)CH—(CH_2)_7COOK + 2KBr$$
$$2CH_3(CH_2)_7CH(C_6H_5O)—(C_6H_5O)CH—(CH_2)_7COOK =$$



$$\begin{array}{l}(C_6H_5O).CH—(CH_2)_7COOK\\ \qquad\quad |\\ (C_6H_5O).CH—(CH_2)_7COOK.\end{array}$$

Under the same conditions, but lower temperature, two other acids are formed:

$$CH_3(CH_2)_7CH(C_6H_5O)—(C_6H_5O)CH-(CH_2)_7COOH = CH_2(C_6H_5O)(CH_2)_7COOH$$

and

$$[3CH_3(CH_2)_7CH(C_6H_5O) + CH(C_6H_5O)(CH_2)_7COOH]$$

The investigation is being continued.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

INTERPRETATIONS OF SOME STEREOCHEMICAL PROBLEMS IN TERMS OF THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCES.

II. HALOGEN SUBSTITUTION IN THE BENZENE NUCLEUS AND IN THE SIDE CHAIN.

BY HARRY SHIPLEY FRY.

Received March 16, 1914.

The present paper, the second of a series[1] relating particularly to the interpretations of some stereochemical problems, is an extension of the principles which have been presented, applied, and discussed in previous papers.[2] The subject matter of this paper, halogen substitution in the benzene nucleus and in the side chain, may be limited appropriately to a discussion and an interpretation of the action of the halogens, chlorine and bromine, upon toluene. There are two very evident reasons for this: (1) Toluene is the simplest derivative of benzene which may be regarded as possessing a side chain, or, perhaps more correctly, a radical, the hydrogen atoms of which are comparable in their chemical behavior to the hydrogen atoms of side chains containing more than one carbon atom. (2) Practically all of the research relating to the problem of substitution in the benzene nucleus and in the side chain has been confined to the action, under various conditions, of chlorine and bromine upon toluene.

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[1] Fry, THIS JOURNAL, 36, 248 (1914).

[2] Some of the earlier papers dealt with problems relating to chemical constitution from the standpoint of electronic formulas and chemical properties. Fry, THIS

A comprehensive idea of the nature and extent of the work upon this subject has been presented by Bancroft from the standpoint of "halogen-carriers" and the electrochemistry of light.[1] The general conclusions, briefly indicated, are as follows: Toluene undergoes substitution either in the nucleus or in the side chain according to the conditions. Schramm[2] found that chlorine or bromine substitute the hydrogen atoms of the side chain at 0° and at higher temperatures *in the sunlight.* In diffused daylight and in the dark a mixture of ortho and para chloro- and bromotoluene results, and a like effect is produced among the higher homologues. Cannizzaro[3] observed that side-chain substitution took place in the dark at the boiling point of toluene. On the other hand, nucleus substitution is induced by the usual carriers such as ferric chloride, molybdenum and antimony pentachloride, iodine chloride, pyridine, and the aluminium-mercury couple. The most recent and noteworthy contribution is the work of Cohen, Dawson, Blockey, and Woodmansey,[4] who found that, at the boiling point of toluene, moist chlorine in the dark produces nuclear substitution to the extent of nearly 90%, whereas in

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JOURNAL, 30, 34 (1908); *Z. physik Chem.*, 76, 385 (1911); THIS JOURNAL, 34, 664 (1912); *Ibid.*, 36, 262 (1914). Other papers presented relationships between the chemical constitution (electronic and dynamic formulas) and the absorption spectra of benzene (Fry, *Z. physik. Chem.*, 76, 398 (1911)), of naphthalene (*Ibid.*, 76, 591 (1911), and of chloro-, bromo-, and iodobenzene (*Ibid.*, 82, 665 (1913)). A theory on fluorescence, with special reference to anthracene and phenanthrene, has also been developed (Fry, *Z. physik. Chem.*, 80, 29 (1912)).

The recent papers of W. A. Noyes (THIS JOURNAL, 35, 767 (1913)); L. W. Jones (*Amer. Chem. J.*, 50, 414 (1913)); Nelson and Falk (THIS JOURNAL, 36, 272 (1914)), and Stieglitz (*Ibid.*, 36, 272 (1914)), present a variety of interesting applications of the electronic conception of positive and negative valences, and also embody references to their other papers upon this subject.

[1] *J. Phys. Chem.*, 12, 417 (1908). See also Cohen and others, *J. Chem. Soc.*, 97, 1623 (1910).

[2] *Ber.*, 18, 350, 606, 1272 (1885); *Ibid*, 19, 212 (1886); *Bull. Acad. Scient. Cracow*, 1898, p. 61.

[3] *Compt. rend.*, 41, 517 (1855).

[4] *Loc. cit.*

the light dry chlorine increases side-chain substitution, yielding on the average about 94% of benzyl chloride. Furthermore, they make this statement: "In so far as the resultant effects are concerned, the action of moisture is opposed to that of light, for this increases the rate of side-chain substitution, and the former accelerates the rate of nuclear substitution."

Various explanations have been proposed to account for these remarkable phenomena. Especially noteworthy are those of Bruner,[1] Bancroft,[2] and Holleman.[3] The fundamental features of these explanations should be noted briefly since they are to be reconsidered from the electronic standpoint of valence.

Bruner maintains that side-chain substitution is due to molecular halogen, while nucleus substitution is effected by halogen atoms or ions which result from the dissociation of the halogen molecules. The velocity measurements of Bruner and Dluska favor this hypothesis, since both side-chain and nucleus substitution processes apparently take place according to the requirements of the equation for a unimolecular change, if the concentration of the bromine is small. For higher concentrations of bromine the values obtained for the unimolecular constant decrease as the reaction proceeds. This is attributed to the removal of the active bromine from the solution by the formation of a perbromide, (HBr_3).

Bruner's idea that nucleus substitution is due to ionic bromine is also maintained by Bancroft, who further assumes that nuclear substitution occurs when *negative* bromine ions are present in excess of the positive bromine ions. This condition is brought about presumably by the partial combination of positive bromine ions with molecular bromine to form complex positive ions, thus:

$$Br_2 = Br^+ + Br^-;\ Br_2 + Br^+ \longrightarrow Br_2.Br^+$$

On the other hand, Bancroft maintains that side-chain substitution takes place under conditions which tend to yield a preponderance of positive bromine ions.

Holleman assumes that side-chain substitution is due to molecular bromine, while nucleus substitution is brought about by a perbromide, HBr_n. The formation of these polyhalogen compounds is actually favored by low temperature and increasing concentration of solution, and these are the conditions which also favor nucleus substitution.

Notwithstanding the various explanations that have been proposed to account for the remarkable phenomena encountered in nucleus and in side-chain substitution, Cohen frankly states[1] "*it must be confessed that nothing definite is known about the mechanism of the process.*" In this connection, it may be of interest to recall a statement made by Brown and Gibson[2] when they formulated a rule for determining whether a given benzene mono-derivative shall give chiefly a meta-di-derivative or a mixture of ortho and para di-derivatives. They stated that their rule is not a law, because "it has no visible relation to any *mechanism* by which substitution is carried out in one way, rather than in another way;" but, since they found it capable of most rigorous application, they concluded that "it must be related in some way to a law, and may be of use in guiding us to the cause of the formation of meta compounds in some cases, and of ortho and para in others." Now the application of the electronic conception of positive and negative valences to the constituent atoms of the benzene molecule and to the principles of the Brown and Gibson rule not only rendered possible an interpretation of the rule but also indicated a *mechanism* according to which substitution must take place in one way rather than in another way.[3] This was a consequence of the evidence, both theoretical and experimental, that in benzene the hydrogen atoms in positions 1, 3, and 5 are negative, while the hydrogen atoms in positions 2, 4, and 6 (relatively speaking) are positive. Accordingly, when substituents are of the same sign or polarity they occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other. This general principle also rendered possible interpretations of the anomalous behavior of various substituted derivatives of benzene.[4] Therefore, it is hoped that the extension of these principles and the electronic conception of valence to the *phenomena* and *conditions* of nucleus and side-chain substitution may afford not only an explanation of the phenomena but also indicate a possible and a probable mechanism of the process.

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[1] *Z. physik Chem.*, **41**, 513 (1902); *Bull. Acad Scient. Cracow*, **1907**, p. 691; *Ibid.*, **1910**, pp. 516 and 560.

[2] *Loc. cit.*

[3] *Rec. trav. chim.*, **27**, 435 (1908).

Nucleus Substitution in Toluene.

Any interpretation of the action of the halogens upon toluene, under the various conditions just noted, must take into account the following facts: (1) The presence of water (moisture), (2) low temperatures, (3) the absence of sunlight (subdued daylight or darkness), and (4) the presence of halogen carriers all favor nucleus substitution, with the consequent formation of *o*- and *p*-chloro- or bromotoluenes. On the other hand, the elimination of water, higher temperatures, and sunlight are the conditions which favor side-chain substitution.

Omitting, temporarily, the discussion of the action of halogen carriers, it is quite important to note that the conditions (1), (2), and (3) which favor substitution in the nucleus are the very conditions which promote the formation, and conserve the stability of, hypochlorous and hypobromous acids (HOX) in which the halogen (X) functions positively. On the other hand, the conditions which favor side-chain substitution, namely heat, light and the absence of water, are those which render hypochlorous and hypobromous acids unstable and promote their action as oxidizing agents. These facts are now to be interpreted as warranting the assumption that substitution in the nucleus in the presence of water (even in minutest traces) is favored by the intermediate formation of hypochlorous of hypobromous acids which on interaction with toluene effect *nucleus substitution of positive halogen.*

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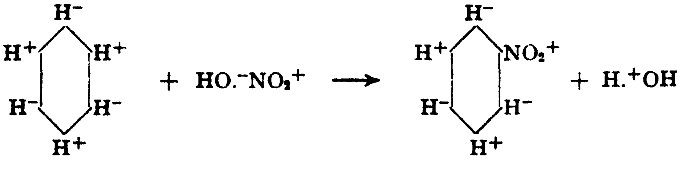
[1] "Organic Chemistry for Advanced Students," 2, 397 (1913).

[2] *J. Chem. Soc.*, 61, 367 (1892).

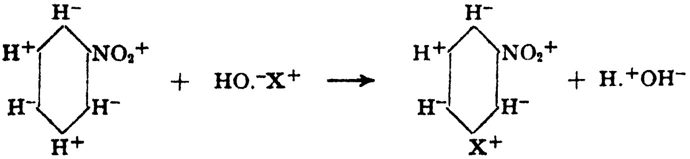
[3] Fry, *Loc. cit.*, THIS JOURNAL and *Z. physik. Chem.*

[4] Fry, *Loc cit.*

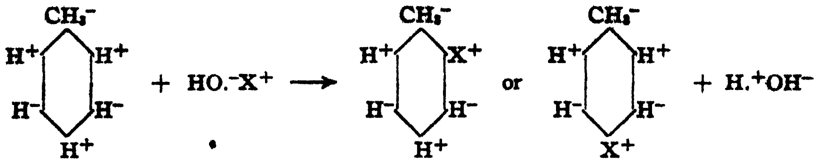
It should be recalled, in this connection, that substituted halogen may function sometimes positively, sometimes negatively. For instance in *o*- and *p*-chloro- or bromonitrobenzenes the halogen atoms are negative, since they are exchanged for negative hydroxyl in double decomposition reactions with aqueous potassium hydroxide, ($K.^+OH^-$). On the other hand, the halogen atoms in the *m*-nitro compounds are regarded as positive for the following reasons: First, the halogen atom is not exchangeable for negative hydroxyl. Second, it is in the meta position to the positive nitro radical, and, according to the electronic formula of benzene, those substituents which are meta to each other are of the same sign or polarity. Third, the substitution of halogen in the nucleus is facilitated if the reagents are not anhydrous. This indicates the possibility of the intermediate formation of the hydroxy halogen acid (HO.X) in which the halogen (X) is positive. Accordingly, the electronic equations for the formation of *m*-chloro- and *m*-bromonitrobenzenes are represented as follows:



$$(X_2 = X.^+X^- + H.^+OH^- \longrightarrow H\,^+X^- + HO.^-X^+)$$



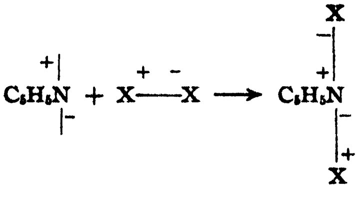
The substitution of positive halogen in toluene proceeds in the same way, but here the halogen assumes the ortho or the para position to the negative methyl radical as follows:



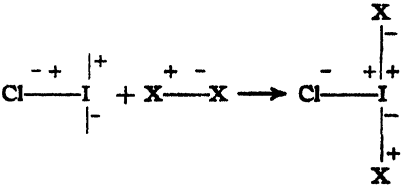
Further evidence of the positive character of the nucleus substituted halogen of toluene is shown by an application of the electronic conception of valence to the Brown and Gibson rule[1] from which standpoint toluene is a derivative of $H.^+CH_3^-$ and not $HO.^-CH_3^+$. Hence substituents ortho or para to the negative methyl radical must be positive. Moreover the substituted halogen atoms are not directly exchangeable for negative hydroxyl and hence are regarded as positive.

The above conclusions are directly opposed to the assumption of Bancroft that nucleus substitution is due to negative halogen. The work of Cohen, showing that moisture increases both the rate and extent of nucleus substitution, also contradicts Bancroft's assumption, if we admit the interaction of the intermediately produced hydroxy-halogen acid ($HO.^-X^+$) upon toluene according to the above electronic formulas and equations.

Since water increases both the rate and extent of nucleus substitution, is it not reasonable to regard water as a halogen carrier? This point of view may throw some light upon the action of halogen carriers in general in effecting nucleus substitution. For instance, pyridine and iodine chloride may be compared to water in that each contains an unsaturated atom which renders possible the formation of addition compounds as follows:



$$\underset{|^-}{\overset{+|}{C_6H_5N}} + \overset{+}{X}\text{——}\overset{-}{X} \longrightarrow \underset{\underset{X}{|^+}}{\overset{\overset{X}{-|}}{\underset{|^-}{\overset{+|}{C_6H_5N}}}}$$



$$\overset{-}{Cl}\text{——}\underset{|^-}{\overset{+\;|^+}{I}} + \overset{+}{X}\text{——}\overset{-}{X} \longrightarrow \overset{-}{Cl}\text{——}\underset{\underset{X}{|^+}}{\overset{\overset{X}{|^-}}{\underset{|^-}{\overset{+|^+}{I}}}}$$

Either of these halogen addition-compounds may dissociate in two ways. Consider the pyridine compound:

$$(1)\ C_6H_5NX^+X^- \longrightarrow C_6H_5NX^- + X^+$$
$$(2)\ C_6H_5NX^+X^- \longrightarrow C_6H_5NX^+ + X^-$$

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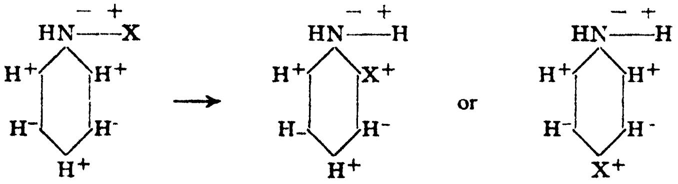
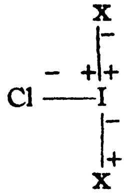
[1] *Loc. cit.*; also Fry, *Z. physiol. Chem.*, 76, 385 (1911).

The previously presented evidence favors dissociation according to equation (1) since it would account for the nucleus substitution of positive halogen. Further evidence is afforded from the standpoint of a comparison of the relative stability of the nitrogen halogen linkings in the halogen addition-compounds. The pyridine halogen compound shows the linkings (N – + X) and (N + — X). The former linking is presumably the least stable and therefore more likely to undergo dissociation, yielding positive halogen. This assumption is warranted by the extreme instability of compounds embodying this linking. For example, W. A. Noyes[1] first showed that the halogen atoms in nitrogen trichloride were positive and bound to negative nitrogen valences. This compound is extremely unstable. The substituted nitrogen halides[2] also embody the linking (N – + X) and are likewise very unstable, exchanging the positive halogen atom for positive hydrogen of the nucleus thereby developing a more stable linking (N — + H) thus



On the other hand the compounds nitrosyl chloride and bromide of the formula $O \overset{-\ \ +}{\underset{-\ \ +}{=\!=\!=}} N \overset{+}{\text{——}} X$ embody the linking (N + — X) and are very stable in comparison with the previously noted compounds containing the N (— + X) linking.[3]



Considering the other typical halogen carrier, $Cl \overset{-\quad +}{\text{——}} \overset{\overset{X}{-}}{\underset{\underset{X}{+}}{\overset{+}{\underset{-}{I}}}}$, it appears that the linking (I + — X) is more stable than (I — + X) This is substantiated by the fact that iodine in iodine chloride and in iodine bromide is positive as evidenced by its interaction with potassium hydroxide, yielding potassium hypoiodite in which the iodine is positive:

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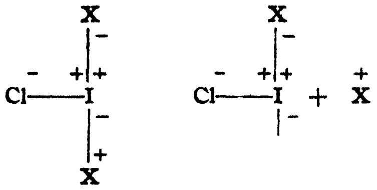
[1] This Journal, 23, 460 (1901).

[2] Fry, *Ibid.*, 34, 667 (1912).

[3] These conceptions are not to be confused with the previously presented idea (Fry, *Z. physik. Chem.*, 76, 387 (1911)) that the polarity of a linking may be reversed through the transposition of electrons, thus giving rise to the conception of electronic isomerism and the possibility of tautomerism of two (or more) electromers, $\overset{+\ \ -}{R\text{——}X} \rightleftharpoons \overset{-\ \ +}{R\text{——}X}$, the existence of either electromer depending upon certain physical conditions. These conceptions were subsequently discussed by Bray and Branch (This Journal, 35, 1445 (1913)) from the standpoint of valence and tautomerism. A recent paper by L. W. Jones develops this conception from the standpoint of intramolecular oxidation and reduction, which renders possible the interpretation of the reactions of numerous nitrogen compounds (*Amer. Chem. J.*, 50, 414 (1913)).

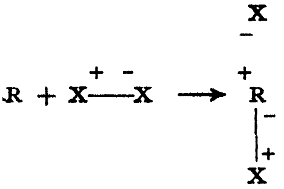
$$\overset{+}{I}\text{—}\overset{-}{X} + 2\overset{+}{K}\text{—}\overset{-\ \ -}{O}\text{—}\overset{+}{H} \longrightarrow \overset{+}{K}\text{—}\overset{-\ -}{O}\text{—}\overset{+}{I} + \overset{+}{K}\text{—}\overset{-}{I} + \overset{+}{H}\text{—}\overset{-\ -}{O}\text{—}\overset{+}{H}$$

Accordingly, the halogen addition compound would maintain the more stable linking, I + — X, and yield the positive halogen ion as follows:

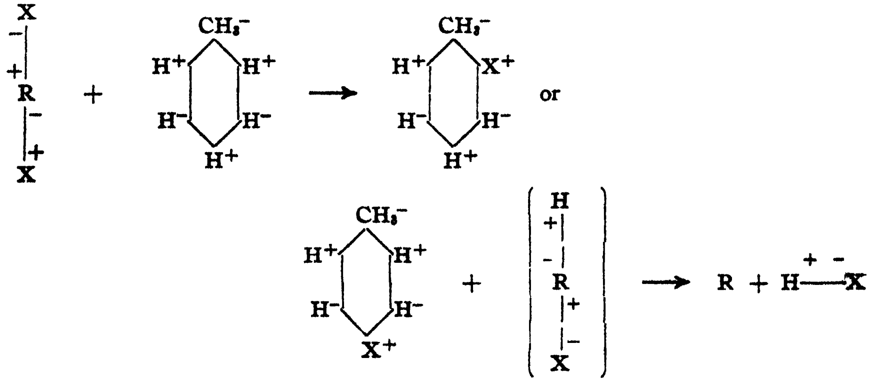


$$\begin{array}{c} X \\ |^{-} \\ \overset{-}{Cl}\text{——}{}^{+}|^{+}\!I \\ |^{-} \\ |^{+} \\ X \end{array} \qquad \begin{array}{c} X \\ |^{-} \\ \overset{-}{Cl}\text{——}{}^{+}|^{+}\!I + \overset{+}{X} \\ |^{-} \end{array}$$

From the above points of view the following mechanism, or cycle of changes, will illustrate the part played by the halogen carrier in effecting the nucleus substitution of positive halogen in toluene. "R" represents any halogen carrier such as water, pyridine, iodine chloride, phosphorus- antimony- and molybdenum-trihalides, or any other compound containing an atom which in uniting with chlorine or bromine X_2 increases its valence from (*n*) to (*n* + 2) as follows:



$$R + \overset{+}{X}\text{——}\overset{-}{X} \longrightarrow \begin{array}{c} \underset{-}{X} \\ \overset{+}{R} \\ |^{-} \\ |^{+} \\ X \end{array}$$

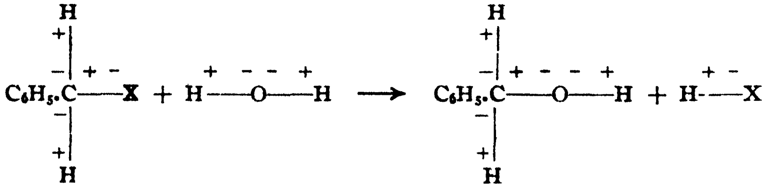


It should be observed that the halogen acid eliminated during the course of the substitution is of the type $\overset{+}{H}\text{——}\overset{-}{X}$, and not $\overset{-}{H}\text{——}\overset{+}{X}$, the latter electromer never having been identified. If neither oxidation nor reduction has occurred during nucleus substitution then the elimination of $\overset{+\;\;-}{H\text{——}X}$ is conclusive evidence that the substituted halogen atom is positive, the reaction having proceeded as indicated above. Halogen carriers of other types may function similarly, *i. e.*, substitute positive halogen and eliminate $\overset{+\;\;-}{H\text{——}X}$. A further discussion of the mechanism of the action of halogen carriers is reserved for a subsequent paper.[1]

Side-Chain Substitution.

In what respects does side-chain substitution differ from nucleus substitution? It has just been shown that nucleus substitution of toluene yields ortho and para halogen toluenes in which the halogen is positive, but when side-chain substitution takes place experimental evidence shows that the substituted halogen atoms are negative. This evidence is as follows:

Benzyl chloride, benzal chloride, and benzotrichloride (or bromides) are readily hydrolyzed by water or by potassium hydroxide, yielding, respectively, benzyl alcohol, benzaldehyde, and benzoic acids. In each of these hydrolyses, chlorine (or bromine) is replaced by negative hydroxyl, which signifies that the substituted halogen atoms of the side chain are negative. The reaction for the hydrolysis of benzyl chloride, or bromide, is typical and may be represented by the following electronic equation·



$$C_6H_5.\overset{\displaystyle H}{\overset{+|}{\overset{-|}{\underset{\underset{\displaystyle H}{+|}}{\underset{-|}{C}}}}}\overset{+\;\;-}{\text{——}}X + H\overset{+\;\;-}{\text{——}}O\overset{-\;\;+}{\text{——}}H \longrightarrow C_6H_5.\overset{\displaystyle H}{\overset{+|}{\overset{-|}{\underset{\underset{\displaystyle H}{+|}}{\underset{-|}{C}}}}}\overset{+\;\;-}{\text{——}}O\overset{-\;\;+}{\text{——}}H + H\overset{+\;\;-}{\text{——}}X$$

This reaction may be reversed by the action of hydrogen halide $(H\overset{+}{\text{——}}-X)$ which converts benzyl alcohol into benzyl halide. This also establishes the fact that halogen atoms substituted in the side chain are negative. An interpretation of these facts must correlate the electronic conception of positive and negative valences with the conditions under which side-chain substitution takes place.

The most significant feature to be noted is that in nucleus substitution the positive hydrogen atoms of toluene are replaced by positive halogen atoms, which change involves neither oxidation nor reduction. But in side-chain substitution, positive hydrogen atoms are replaced by negative halogen atoms. In other words, side-chain substitution involves oxidation and reduction: the carbon-hydrogen linking (C — + H) is changed to a carbon-halogen linking (C + — X). The negative valence of carbon is oxidized to a positive valence and this change could not occur unless the substituting agent is reduced. Now the substituting agent (molecular halogen, X_2) must undergo dissociation into positive and negative halogen atoms, and the negative halogen naturally combines with the positive hydrogen of the side chain to form hydrogen halide, $\overset{+}{H}\text{—}\overset{-}{X}$. This necessitates the conclusion that *the remaining positive halogen atom (nascent halogen)*[1] *acts as the oxidizing agent which converts the negative valence of carbon to a positive valence.* The positive halogen atom is thereby reduced to a negative halogen atom which is then bound by the positive valence of carbon. The changes thus involved in side-chain substitution may be represented as follows:

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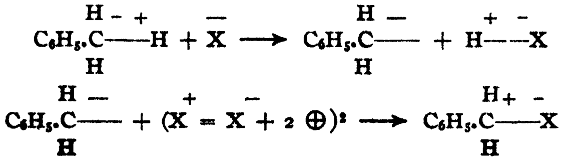
[1] Any halide functioning as a halogen carrier may conform to the above scheme, since its halogen atoms may be unsaturated and hence combine with other halogen atoms just as the iodine atom in iodine chloride lends itself to the formation of iodine trichloride.

$$X_2 = \overset{+}{X}\overset{-}{\text{—}}X \longrightarrow \overset{+}{X} + \overset{-}{X}.$$



$$C_6H_5.\underset{H}{\overset{H}{C}}\overset{-\ +}{\text{——}}H + \overset{-}{X} \longrightarrow C_6H_5.\underset{H}{\overset{H}{C}}\overset{-}{\text{——}} + \overset{+}{H}\overset{-}{\text{——}}X$$

$$C_6H_5.\underset{H}{\overset{H}{C}}\overset{-}{\text{——}} + (\overset{+}{X} = \overset{-}{X} + 2\,\oplus)\text{[2]} \longrightarrow C_6H_5.\underset{H}{\overset{H}{C}}\overset{+\ -}{\text{——}}X$$

The remaining hydrogen atoms of the side chain undergo substitution in precisely the same manner.

Having indicated a mechanism which accounts for the substitution of negative halogen in the side chain and thereby involves an oxidation of negative valences of carbon to positive valences, it is now desirable to account for the fact that nucleus substitution does not involve oxidation while side-chain substitution does.

It has been observed that the conditions which promote nucleus substitution (omitting halogen carriers which have been considered) are low temperatures and the absence of sunlight. These are the conditions which promote the formation and conserve the stability of hypochlorous and hypobromous acids, that is, prevent their decomposition as oxidizing agents. On the other hand the chief conditions promoting side-chain substitution (heat and sunlight) are the very factors which render these hydroxy-halogen acids unstable and effect their decomposition as oxidizing agents. Let us now inquire into the most significant feature of these changes. If hypochlorous or hypobromous acids are heated or exposed to the action of sunlight, oxygen is evolved and hydrogen chloride or bromide is formed ($2HOX \longrightarrow 2HX + O_2$). The halogen in HOX is positive; in HX it is negative. Hence it follows that heat, and especially *the photochemical action of light, effect the conversion of positive halogen to negative halogen, thus,* $X^+ \longrightarrow X^- + 2\oplus$. This is the oxidation process upon which the elimination of oxygen from HOX depends.[1] Now the substitution of halogen in the side chain, as described above, is also an oxidation process, since it likewise involves the essential change, $X^+ \longrightarrow X^- + 2\oplus$, induced either by heat or by photochemical action. Thus the conditions which favor and promote side-chain substitution are correlated with the fact that positive hydrogen atoms of the side chain are substituted by negative halogen atoms, which involves the reduction of positive halogen to negative halogen, and the consequent oxidation of negative valences of carbon to positive valences which bind the negative halogen atoms.[2]

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[1] An interpretation, from the electronic standpoint, of the nascent state and its relation to oxidation and reduction phenomena has been given in a previous paper (Fry, This Journal, 36, 262 (1914)).

[2] Positive halogen atoms act as oxidizing agents since they tend to become negative by acquisition of electrons. In terms of the atomistic conception of electricity, the acquisition of negative electrons is equivalent to the liberation of the so-called "positive electrons" which convert negative valences into positive valences.

In this paper some fundamental distinctions between nucleus and side-chain substitution have been developed and interpretated in terms of positive and negative valences. A common occurrence, however, should not be overlooked, namely, that in most substitution reactions it is practically impossible to so limit and regulate the conditions that the *sole* reaction taking place will be either nucleus substitution or side-chain

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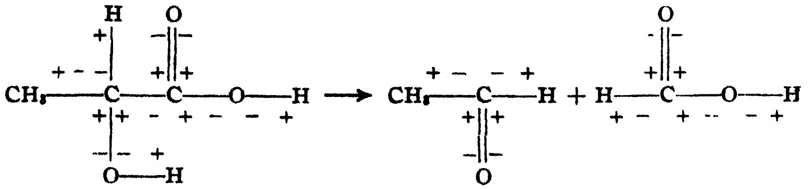
[1] Electronic equations for this change may be indicated in two ways: The first has been described in detail (Fry, THIS JOURNAL, 36, 267 (1914)). The second is from the standpoint of intramolecular oxidation and reduction (L. W. Jones, *Loc. cit.*) and may be represented as follows:

$$2\mathrm{H}\overset{+\ -}{\text{———}}\mathrm{O}\overset{-\ +}{\text{———}}\mathrm{X} \longrightarrow 2\mathrm{H}\overset{+\ -}{\text{———}}\mathrm{O}\overset{+\ -}{\text{———}}\mathrm{X} \longrightarrow 2\mathrm{HX} + (2\overset{+\ -}{\mathrm{O}} \overset{-\ +}{=} \mathrm{O} \underset{-\ +}{\overset{+\ -}{=\!=}} \mathrm{O} = \mathrm{O}_2)$$

Either way of interpreting the change involves the reduction of positive halogen (an active or nascent form of halogen) to negative halogen and the consequent oxidation of negative valences of oxygen to positive valences.

[2] In this connection it may be of interest to note and to correlate another of many reactions in which light changes negative valences of carbon to positive valences. Euler and Ryd (*Biochem. Z.*, 97, 106) have shown that lactic acid under the influence of ultraviolet rays evolves carbon dioxide. The electronic interpretation depends upon the fact that lactic acid readily yields aldehyde and formic acid as follows:



Now in order that formic acid, in which three of the carbon valences are positive and one is negative, may yield carbon dioxide, in which the four valences of carbon are positive, the one negative valence of carbon in formic acid must be oxidized to a positive valence. This change takes place when formic acid is catalytically or photochemically substitution. In other words, the formation of ortho and para halogen toluenes, in which the halogen atoms are positive, and the introduction of negative halogen into the side chain, may proceed as simultaneous independent chemical changes. As previously noted the former process does not involve oxidation and reduction while the latter does. These facts are readily correlated with another general property characteristic of benzene on the one hand, and characteristic of aliphatic hydrocarbons (comparable to side chains) on the other hand. *Benzene resists oxidation while the aliphatic hydrocarbons and the side chains are generally more susceptible to oxidation.*

Finally, it is not impossible to conceive that, under certain conditions, which are not as yet determined and interpreted, a positive hydrogen atom of the benzene nucleus may be replaced by a negative halogen atom (or *vice versa*) which is characteristic of side-chain substitution, involving oxidation and reduction. Such a condition, however, does not invalidate the interpretations presented in this paper which are correlated with the experimental facts, the conditions of substitution, and the chemical properties of ortho and para halogen toluenes, and the side-chain substitution products.

In concluding, the relations between the interpretations given in this paper and the substitution hypotheses of Bruner, Bancroft, and Holleman should be reconsidered briefly.

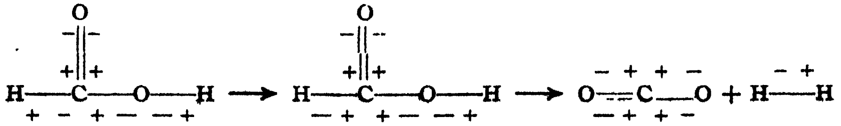
Bruner's idea that nucleus substitution is due to halogen atoms, while side-chain substitution is due to molecules, thus,

$$C_6H_5CH_3 + 2Br \longrightarrow BrC_6H_4CH_3 + HBr,$$
$$C_6H_5CH_3 + Br_2 \longrightarrow C_6H_5CH_2Br + HBr,$$

fails to take into account the fact that nucleus substitution (former equation) does not involve oxidation and reduction while side-chain substitution (latter equation) does.

Bancroft's assumption that nucleus substitution is due to negative halogen atoms is not in agreement with the evidence, both theoretical and experimental, that the ortho and para substituted halogen atoms of toluene are positive. His other assumption that the halogen substituted in the side chain is positive is also contradicted by the fact that the halogen

decomposed, yielding carbon dioxide and hydrogen according to the following electronic equation:

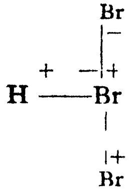


$$\mathrm{H{-}\overset{O}{\underset{}{C}}{-}O{-}H} \longrightarrow \mathrm{H{-}\overset{O}{C}{-}O{-}H} \longrightarrow \mathrm{O{=}C{=}O} + \mathrm{H{-}H}$$

A further discussion of photochemical changes from this standpoint is reserved for a subsequent paper.

atoms in benzyl chloride, benzal chloride, and benzotrichloride (or bromides) are negative, since they are readily exchanged (without oxidation or reduction) for negative hydroxyl. It is true, however, that positive halogen atoms are the active substituting agents in side-chain substitution, but only by virtue of their oxidizing action and consequent reduction to negative halogen (photochemical action) as previously described.

Finally, Holleman has stated[1] "Il est démontrè, que l'hypothèse, suivant laquelle le noyau est attaqué par des molécules HBr_n, tandis que la châine latérale l'est par les molécules de brome, a quelque vraisemblance; cependant un nombre de difficultés devoint encore être levées, avant qu'elle puisse servir à expliquer les phénomènas observés." The very plausible interpretation of the nucleus bromination of toluene through the action of the intermediately formed HBr_n may be readily correlated with the interpretation of nucleus substitution and the action of halogen carriers as presented in this paper, provided HBr_n be regarded as



$$\overset{+}{\mathrm{H}}\overset{-}{\text{——}}\overset{\overset{\mathrm{Br}}{|-}}{\underset{\underset{\mathrm{Br}}{|+}}{\overset{|+}{\mathrm{Br}}}}$$

. But Holleman's idea of side-chain substitution is subject to the criticism that it also fails to recognize the side-chain substitution process as an oxidation and reduction phenomenon depending upon the reaction, $X^+ \longrightarrow X^- + 2\oplus$, previously considered.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

STUDIES ON ENZYME ACTION. X. THE LIPOLYTIC PROPERTIES OF HUMAN DUODENAL CONTENTS.

BY K GEORGE FALK

Received February 27, 1914

The enzymes of the digestive tract play an essential part in the changes which foodstuffs must undergo before they can be utilized in the animal body. Within recent years it has become possible to remove the contents of the upper part of the intestinal tract of human beings directly and to study their properties. Much valuable information with regard to the enzymes present has already been obtained in this way. The results to be described in this paper deal with the lipolytic properties of duodenal contents obtained under varying conditions and tested in different ways. It is believed that a detailed study of the behavior of one enzyme may at the present time be more useful than the routine examination for the ordinary digestive enzymes.

[1] *Loc. cit.*

The technique developed by Einhorn[1] and by Gross[2] and recently improved by Palefski,[3] which consists essentially in the swallowing of a soft rubber tube provided at its lower end with a perforated metallic capsule, allowing this to reach the duodenum, and subsequent aspiration of the duodenal contents by means of a suitable pump, has been used in a number of investigations. The enzymes of the duodenal contents have been studied by Einhorn and Rosenbloom,[4] Hess,[5] Crohn[6] and Chase and Myers.[7]

The results which were obtained in this investigation may be divided into several groups. Although they were not obtained in this order in the actual experimental work, for convenience of presentation they will be given in the simplest form. The general grouping comprizes: first, the results which, so far as present evidence extends, may be looked upon as the normal action on fats; second, under somewhat altered conditions, lipolytic activity differing markedly from that given in the first group; third, some evidently abnormal, or preferably, unexpected lipolytic behaviors of duodenal contents; fourth, the action of duodenal lipases in the presence of dilute solutions of the chloride, bromide, iodide, and fluoride of sodium; and fifth, the effect of a number of neutral inorganic and organic substances upon the duodenal lipases.

The method of obtaining the duodenal contents has frequently been described and will not be given here in detail. The Einhorn tube was used in every case except with Patient P and was allowed to remain over night. Whether or not food was taken before removing the contents will be stated in the appropriate places. With Patient P, the Palefski tube was used in the manner described by him. Toluol was added to the contents as soon as possible after these were obtained, generally within fifteen minutes, and the solutions for the tests made up at once. On a few occasions the tests were repeated after an interval of several days, during which the specimens remained in the ice-chest; but the results showed only inconsiderable differences from those obtained in the immediate tests on the same samples.

In the course of a study of the lipolytic properties of the castor bean, two lipases, which showed distinct differences in their action, were found to be present.[8] Under comparable conditions of testing, one of these set free more acid from ethyl butyrate than from triacetin (glyceryl triacetate) while the other set free more acid from triacetin than from ethyl butyrate. Moreover, since Loevenhart[1] had found a difference in the action of extracts of various animal organs on these same esters, it was decided to test the lipolytic activity of every sample of duodenal contents with the two esters.

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[1] *Med. Rec.*, 77, 98 (1910).

[2] *New York Med. J.*, 91, 77 (1910).

[3] *Ibid.*, Oct. 18, 1913.

[4] *Arch. Intern. Med.*, 6, 666 (1910); *Intern. Beitr. z. Path. u. Ther. d. Ernährungsstöro.* 2, No. 2 (1910).

[5] *Am. J. Dis. Child.*, 3, 304; 4, 205 (1912); 5, 268 (1913); *Arch. Intern. Med.*, 10, 37 (1912).

[6] *Am. J. Med. Sci.*, 145, 393 (1913).

[7] *Arch. Intern. Med.*, 12, 628 (1913).

[8] THIS JOURNAL, 35, 1904 (1913).

The experimental methods were essentially the same as those used in the castor bean work. 0.5 cc. of the duodenal contents were diluted to 25 cc. with water or the solution to be tested in a 100 150 cc. Erlenmeyer flask. Six of these solutions were made up for each set of tests, 1.0 cc. neutral ethyl butyrate was added to each of two, 0.5 cc. neutral triacetin to each of two, 0.5 1.0 cc. toluol to all, and all shaken thoroughly and placed in an incubator kept at 38-40° for 24 hours. At the end of this time they were titrated with standard sodium hydroxide solution, very nearly 0.1 normal, with five to ten drops of a 1% phenolphthalein solution in 95% ethyl alcohol as indicator. Ethyl butyrate and triacetin in similar amounts were allowed to act for the same length of time with 25 cc. water, or solution, and the acid produced without the presence of duodenal contents determined in the same way. The difference between the mean of the titrated values of the duodenal contents-solution-ester mixtures and the sum of the means of the titrated values of the duodenal contents–solution mixtures and of the ester-solution mixtures, expressed as cc. of 0.1 *N* solution, is a measure of the amount of acid set free by the action of the duodenal contents upon the esters. The figures in the following tables are all strictly comparable, except for a few in Tables IV and V as indicated in the footnotes.

In Table I are given the results obtained with duodenal contents diluted with water. The first ten specimens were withdrawn between one and three hours after the patient had been given a glass of milk. The eleventh specimen (A) was obtained an hour after three lumps of sugar and a glass of water had been taken, and the last three, a few minutes after taking a glass of 0.2% hydrochloric acid. In the table, Column 1 signifies the patient and the treatment prior to the aspiration of the duodenal contents; Column 2, the amount of duodenal contents obtained; Column 3, their color; Columns 4 and 5, the actions obtained in terms of 0.1 *N* acid (corrected for the blanks) produced from 1.0 cc. ethyl butyrate and 0.5 cc. triacetin, respectively, in 24 hours at 38–40°, by 0.5 cc. contents in 25 cc. water; and the last column, the ratios obtained by dividing the number of cc. of 0.1 *N* acid set free from triacetin by the number of cc. set free from ethyl butyrate. The contents were themselves either neutral or slightly acid toward phenolphthalein. As a rule, after milk had been taken, they contained a considerable amount of white coagulated material. In the other cases they were only slightly turbid.

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[1] *J. Biol. Chem.*, 2, 429 (1907).

TABLE I.—THE LIPOLYTIC ACTIONS OF DUODENAL CONTENTS OBTAINED AFTER TAKING FOOD.

Case.	Amount. Cc.	Color.	Cc. 0.1 N acid set free from Ethyl butyrate.	Triacetin.	Ratio. $\frac{\text{Acid from Triac.}}{\text{Acid from Et. Bu.}}$*
A (milk)........	25.0	Yellow	7.46	12.21	1.64
A (milk)........	19.2	Yellow	5.09	8.32	1.63
C (milk)........	9.5	Colorless (Green tinge)	2.33	7.07	3.03
J (milk).........	15.0	Yellow	4.56	11.20	2.46
K (milk)........	13.0	Colorless	2.35	7.71	3.28
P (milk)........	34.0	Yellow	0.73	1.59	2.17
I (milk).........	35.0	Colorless	2.39	8.03	3.36
D (milk)........	24.0	Yellow-brown	0.45	1.05	2.33
M (milk)........	10.5	Yellow	0.80	1.26	1.58
O (milk)........	17.0	Yellow-green	2.45	6.36	2.60
A (sugar)........	11.0	Colorless (Green tinge)	1.40	3.82	2.73
E (HCl).........	3.0	Yellow	1.26	2.05	1.63
F (HCl).........	3.0	Colorless	1.41	3.65	2.59
H (HCl)........	30.0	Colorless	1.59	5.61	3.53

The volume of juice and the lipolytic activity per unit volume varied greatly, nor was there any regularity in the relation between the two. It is, however, evident that duodenal contents obtained under these conditions contained an enzyme or enzymes which set free much more acid (58–256%) from triacetin than from ethyl butyrate.

In marked contrast to these results are the figures presented in Table II. The specimens, the actions of which are here recorded, were obtained after at least twelve hours abstinence from food. Some of the patients drank a little water a few minutes before the duodenal contents were aspirated.

TABLE II.—THE LIPOLYTIC ACTIONS OF DUODENAL CONTENTS OBTAINED WITHOUT TAKING FOOD.

Case.	Amount. Cc.	Color.	Cc. 0.1 N acid set free from Ethyl butyrate.	Triacetin.	Ratio. $\frac{\text{Acid from Triac.}}{\text{Acid from Et. Bu.}}$*
C.........	10.5	Yellow	3.59	1.88	0.52
P.........	4.0	Yellow	1.32	1.06	0.80
L.........	3.0	Yellow	0.36	0.37	1.03
B........	10.5	Yellow	0.28	0.27	0.96
A........	8.2	Yellow	0.25	0.15	0.60

The significant fact which appears from these results is that the actions toward ethyl butyrate are distinctly greater than those toward triacetin when compared with the results of Table I. In every case, at least as much acid was liberated from ethyl butyrate as from triacetin, and in one case almost twice as much. As regards volume and action per unit volume, the same irregularities appear as in the first group. As compared with each other, apparently more duodenal juice may be aspirated than in inanition. However, the results are too few in number to permit definite conclusions with regard to these questions to be drawn.

In Table III are presented some apparently exceptional results.

TABLE III.—SOME UNUSUAL OR ABNORMAL LIPOLYTIC ACTIONS OF DUODENAL CONTENTS.

Case.	Amount. Cc	Color.	Cc. 0.1 *N* acid set free from		Ratio. $\frac{\text{Acid from Triac.}}{\text{Acid from Et. Bu.}}$
			Ethyl butyrate.	Triacetin.	
C (milk).....	11.0	Yellow	2.19	1.68	0.77
G (milk).....	20.0	Yellow	1.73	1.38	0.80
H (HCl)......	8.2	Yellow-green	1.75	1.41	0.80
I (water)......	3.7	Light brown	1.50	6.22	4.15

The first three cases of Table III might be included in Table I, but the results obtained are typical of the duodenal contents from fasting individuals, although these patients had taken milk or hydrochloric acid. Again, the fourth specimen, although obtained after water had been taken, behaved very much like the specimens obtained after taking food.

A few words, with regard to the pathological conditions under which some of the specimens were obtained, may be of interest. Patients E, F and H, Table I, were convalescing from typhoid fever. The duodenal contents of Patient G, also a typhoid convalescent, displayed a different type of lipolytic behavior, shown in Table III, from those of E, F, and H, under similar conditions with hydrochloric acid. The duodenal contents of G were therefore tested again a week later after drinking milk, but the same unusual results were obtained as before (Table III). Patients J and K, Table I, suffered from duodenal ulcer at the time the specimens were obtained, but no unusual results were found for the lipolytic actions. The diagnosis for Patient C was nervous dyspepsia. When he was admitted to the hospital the results given in Tables II and III were obtained. With milk, or after fasting, the type of action was the same and different from the action generally obtained after taking food. One week later, his condition had improved, and the lipolytic action of his duodenal contents, aspirated after drinking milk, showed the usual relations (given in Table I). The duodenal contents of Patient I, obtained either after taking milk or water, showed no difference in behavior (Tables I and III). An operation for nephrolithotomy was performed later. As for the remaining patients and others who furnished duodenal contents, there was no evidence of digestive disturbance to call for further remark or description.

It is evident, therefore, that abnormal results may be obtained from time to time even if all the conditions for obtaining the desired secretions are apparently satisfactory. For diagnostic purposes, the possibility of these exceptional behaviors must be kept in mind.

The results so far presented show two types of lipolytic activity in the duodenal contents, or in other words, two lipases. One of these, more active toward triacetin, is most in evidence when food is taken, the other, which acts chiefly upon ethyl butyrate, appears to predominate in the absence of food. There is no reason to suppose that each lipase acts only on one ester. On the contrary, it is more probable that each lipase acts on both esters, but that one exerts greater action on one ester and the other greater action on the other ester. It is extremely suggestive that the lipase most active upon triacetin, which like the fats is a triglyceride, is the one found after the ingestion of food. It seems probable that this lipase predominates in the pancreatic secretion. Support is given to this view by the work of Loevenhart,[1] already referred to, in which extracts of the pancreas of animals were found to be more active toward triacetin than toward ethyl butyrate.

It may be of interest to compare these results with those obtained by others. So far as the writer is aware, no comparative study of the action of human duodenal contents, obtained with the duodenal pump, on two or more esters has been made. Most of the published investigations have taken up the enzymic activities more from the point of view of practical diagnosis. The investigation of Einhorn and Rosenbloom[1] treated of the different methods for causing the flow of pancreatic juice by various foods and drugs and presented much valuable information. The study by Bradley[2] of human pancreatic juice obtained from a fistula is of interest in this connection. Very much more action was observed with olive oil than with ethyl butyrate. As the result of a number of experiments with added substance, it was concluded that only one lipase was present and acted on the two esters.

The results presented in this paper with duodenal contents obtained after food had been taken (Table I) showed strong action toward triacetin and much less toward ethyl butyrate. Here, evidently, pancreatic juice (and bile) exerted an action similar to that observed in ordinary fat digestion. Triacetin was used in place of a fat or oil since it is readily soluble in water and comparable conditions could be obtained in different experiments. The use of fat or oil would have involved the preparation of an emulsion for every set of experiments with the possibility of varying conditions at different times. Furthermore, it was realized that it would be extremely difficult to approach *in vitro* the conditions of lipolysis *in vivo*, such as constant stirring and mixing of the reacting mass, continual addition of fresh enzyme, continual removal of the products of the reaction, etc. It was therefore decided to use comparable conditions, as simple as possible, for testing the activities.

[1] *Loc. cit.*

[2] *J. Biol. Chem.*, 6, 141 (1909).

The lipolytic activities observed when no food had been taken, and any considerable quantity of pancreatic juice and bile, therefore, probably absent, indicated the presence of a different lipase in these specimens. It may be suggested that this lipase is present in intestinal juice, which as is known is secreted in some quantity when the intestinal walls are mechanically irritated.[1] This may well be caused by the capsule and tubing of the duodenal pump. That intestinal juice contains lipase has been shown among others by Boldyreff[2] and by Jansen[3] in experiments with dogs in which fistulas had been established. Unfortunately no experiments with different esters are presented which might throw light on the possibility of the lipase of intestinal juice acting as indicated here.

In considering the results obtained with the two esters, ethyl butyrate and triacetin, it must be remembered that the experimental conditions used were chosen rather arbitrarily. It is probable that a more complete study of these, and also of other esters, would give more satisfactory conditions for comparing and studying the activity of the two lipases in duodenal contents.

In many cases it has been found that neutral substances, organic as well as inorganic, modify profoundly the actions of various enzymes. Since the present paper is concerned only with lipases and their actions, it may suffice to mention a few of the investigations which have concerned themselves with the actions of neutral substances on the activities of lipases before presenting the results obtained with human duodenal contents. Loevenhart and Pierce[4] observed a very marked inhibiting action of sodium fluoride and hydrofluoric acid on the lipolytic activities of extracts of various animal organs on different esters and oils for all except the most dilute solutions of fluoride. These had an accelerating action. Terroine[5] showed, with pancreatic juice obtained from dogs with fistulas, that this inhibition was not limited to the fluoride of sodium but was also shown by the chloride, bromide, and iodide, but to a much less extent both on simple esters and on olive oil. In a previous paper of this series,[6] the action of a number of neutral salts on the lipolytic activity of a castor bean preparation toward ethyl butyrate was described. The results paralleled very closely those obtained by Terroine with an animal lipase on the same ester. In particular, the inhibiting action of equivalent solutions of the sodium salts, chloride, bromide, iodide, fluoride, increased in the order named, and for any one salt with increasing concentration. The other results reported there will not be given in detail and other work will not be described further. It may be mentioned, however, that the apparently contradictory results obtained in many investigations of the action of neutral substances particularly, on lipases and probably on enzymes in general, will be found, in most cases to be due to the different experimental conditions which were used. For instance, the ester used may have been different and may account for the different results obtained; the amount of water plays a part; the formation of insoluble substances such as insoluble soaps if a salt of a metal, such as calcium, and an oil are used; the neutralization of the lipase solution initially, involving the addition of an indicator generally dissolved in alcohol and alkali, in this way forming a salt, etc.; each action small, perhaps, but unquestionably affecting the lipolytic behavior observed.

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[1] E. H. Starling, *Principles of Human Physiology*, p. 788 (1912).

[2] *Z. physiol. Chem.*, **50**, 394 (1907).

[3] *Ibid.*, **68**, 400 (1910).

[4] *J. Biol. Chem.*, **2**, 397 (1907).

[5] *Biochem. Z.*, **23**, 429 (1910).

[6] THIS JOURNAL, **35**, 601 (1913).

The figures presented in Table IV were obtained in the same way as those in the previous tables. The results are given for water and for the four halides of sodium for 0.1 molar concentration. As before, the actions are expressed as the number of cc. of 0.1 *N* acid liberated in 24 hours at 38–40° by 0.5 cc. duodenal contents in 25 cc. water or solution from 1.0 cc. ethyl butyrate or 0.5 cc. triacetin.

TABLE IV.—THE LIPOLYTIC ACTIONS OF DUODENAL CONTENTS IN 0.1 MOLAR SODIUM HALIDE SOLUTIONS.

Results with ethyl butyrate.

Patient.	H_2O.	0.1 M NaCl.	0.1 M NaBr.	0.1 M NaI.	0.1 M NaF.
J	4.56	3.60	3.36	0.40	0.72
K	2.35	2.13	..	0.26	0.37
P	1.58	1.24	..	..	0.54
I[1]	3.66	2.88	1.66	0.45	0.70
P	0.73	0.57	0.59	0.61	0.19
G	1.75	1.31	0.86	0.46	0.46

Results with triacetin.

Patient.	H_2O.	0.1 M NaCl.	0.1 M NaBr.	0.1 M NaI.	0.1 M NaF.
J	11.20	10.85	10.33	1.42	0.68
K	7.71	8.17	..	1.15	0.21
P	3.07	3.77	..	2.94	0.67
I[1]	12.02	12.10	9.08	0.77	0.71
P	1.59	1.62	1.48	0.89	0.33
G	1.41	1.27	1.03	0.38	0.77

A different behavior was found for the actions of these salt solutions with the two esters, and therefore, presumably, the two lipases were affected differently. With ethyl butyrate, the sodium chloride retarded the actions distinctly, the bromide somewhat more markedly as a rule, while the iodide and fluoride showed the greatest retardations. The iodide exerted greater inhibiting action than the fluoride in the greater number of cases. Terroine found the retardation to increase in the order, chloride, bromide, iodide, fluoride, with an animal lipase; while the same order was found with the castor bean lipase.

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[1] 0.2 cc. duodenal contents, 48 hours action.

With triacetin, sodium chloride (of the concentration indicated) had practically no effect or a distinct accelerating action, while the bromide, iodide, and fluoride exerted greater inhibition in the order named (one result for fluoride showed less inhibition than for iodide, but against this must be placed the five showing the opposite). These actions correspond very closely to the results of Terroine with animal pancreatic juice on triacetin and also with unpublished work with castor bean and soy bean lipases. In all these cases, 0.1 molar sodium chloride solution either had no action or increased the hydrolytic action on triacetin; while with the other halides, distinct inhibition, which increased in the order bromide, iodide, fluoride, was observed.

TABLE V.— THE LIPOLYTIC ACTIONS OF DUODENAL CONTENTS IN SOME NEUTRAL SALT AND ALCOHOL SOLUTIONS.

Results with ethyl butyrate.

Patient.	H_2O.	1 M KCl	1 M KBr	1 M KI	1 M KF.	0.1 M NaF.	1 M NaCl.
A	7.46	.	..	..	..	0.88	4.66
A	5.09	2.69	2.45	0.08	0.41	..	..
		0.05 M $MgSO_4$.	0.005 M $MnSO_4$.				
I[1]	3.66	1.90	1.60	..	..	..	..
				1 M CH_3OH.			
D[2]	0.90	0.73	..	0.59	..	0.23	0.75
		0.1 M CH_3OH	0.1 M C_2H_5OH.				
M	0.80	1.93	2.09	..	..	0.25	..
					1 M C_2H_5OH.		
O	2.45	2.62	2.11	1.70	1.52	.	..
P	0.73	0.60	0.50	..	..	..	..
						1 M NaI.	
G	1.75	..	..	..	.	0.04	0.64

Results with triacetin.

	H_2O.	1 M KCl	1 M KBr.	1 M KI.	1 M KF.	0.1 M NaF.	1 M NaCl.
A	12.21	..	..	..	..	1.57	8.15
A	8.32	5.42	3.75	0.06	0.48	..	..
		0.05 M $MgSO_4$.	0.005 M $MnSO_4$.				
I[1]	12.02	7.03	7.40	.	..	.	..
				1 M CH_3OH.			
D[2]	1.56	1.29	..	1.21	..	0.20	2.32
		0.1 M CH_3OH.	0.1 M C_2H_5OH				
M	1.26	3.15	2.56	..	..	0.30	..
					1 M C_2H_5OH.		
O	6.36	0.76	0.65	0.86	0.99	..	..
P	1.59	1.37	1.13	.		..	..
						1 M NaI.	
G	1.41	..	..	..	.	0.08	0.41

[1] 0.2 cc. duodenal contents; 48 hours action.

[2] 48 hours action.

Table V summarizes the results of a number of miscellaneous experiments with different salt and alcohol solutions of the indicated concentrations under the same conditions as before.

The results of Table V will be discussed together for the two esters since essentially the same relations appear. The molar solutions of the potassium and sodium halides all showed very marked inhibiting actions, the inhibition increasing in the order chloride, bromide, fluoride, iodide for both esters. The order fluoride, iodide is interesting again in comparison with the results discussed in connection with Table IV where the more dilute solutions of the same salts were considered.

Several experiments were made using magnesium and manganous sulfates. The concentrations chosen were those which had given the most marked and most readily measured accelerations with the lipolytic activity of the castor bean preparation. The duodenal contents, however, did not show any acceleration either in the action on ethyl butyrate or on triacetin, but on the other hand showed very marked retardations in both cases.

A number of results are presented with 0.1 molar and 1.0 molar solutions of methyl alcohol and ethyl alcohol. In one case, Patient M, very strong accelerations toward both esters were observed with the 0.1 molar solutions of the two alcohols; in the other cases the retardations were very marked, except for the 0.1 molar methyl alcohol solution with ethyl butyrate for Patient O where a small acceleration was observed. The results with Patient M appear to be exceptional and due to unknown causes. The general action of the alcohols may, for the present, be looked upon as retarding the lipolysis, in agreement with the results with castor bean lipase.[1]

The results summarized in Tables IV and V are of interest from the purely scientific point of view in connection with the study of the chemical properties and reactions of lipases. At the same time, these accelerations and retardations of the enzymic activity due to the neutral salts suggest some questions and problems of more direct practical importance. The bromides and iodides of sodium and potassium have extensive therapeutic use, and it may be asked whether the continued administration of these, even in small quantities, will not exert a deleterious influence on digestive processes, in connection with fat digestion. Especially would this be true for the iodides, which *in vitro* inhibit so markedly the lipolytic activity of duodenal contents. The action of alcohol may possibly be harmful in a similar way. The study of the enzymic activities of the duodenal contents of a large number of suitable cases might throw some light on these questions.

The writer wishes to take this opportunity to thank Dr. William G.

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[1] THIS JOURNAL, 35, 616 (1913).

Lyle, Director of this laboratory, Dr. Mortimer Warren, Pathologist of Roosevelt Hospital, and the different members of the House Staff of the hospital, for obtaining the specimens used in this investigation. Thanks are due Dr. I. Greenwald of this laboratory for helping to prepare the results of this investigation for publication.

Summary.

The lipolytic activity of human duodenal contents was tested in a number of cases under varying conditions.

Two lipases were present in the duodenal contents. One of these, found as a rule after ingestion of food, was, under certain definite experimental conditions, more active toward triacetin than toward ethyl butyrate; the other, present when no food had been taken, was more active toward ethyl butyrate than toward triacetin. The importance of these two lipases in diagnostic work was pointed out.

Lipases, showing similar differences in their actions on the two esters, have been shown to be present in castor beans, and also by Loevenhart in extracts of the pancreas and liver of various animals.

The effect of a number of neutral salts and alcohols in different concentrations on the activity of the duodenal contents on the two esters was studied.

CORRECTION.

In referring to Mr. A. F. McLeod's paper as abstracted in the *Chemical Abstracts* in my paper on "Some Organic Preparations" (THIS JOURNAL, **36**, 532), I find that I have not interpreted correctly the statement "calcium or sodium hydroxide solution of 0.1 %." This percentage, I find, refers to an aqueous solution; whereas my percentages were referred to the aldehyde used. It follows, therefore, that the experimental conditions in each case were different. I take this opportunity of correcting my statement in my paper alluded to above, and expressing my regrets to Mr. McLeod.

L. P. KYRIAKIDES.

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The Scientific Work of Morris Loeb, edited by THEODORE W RICHARDS, Professor of Chemistry and Director of the Wolcott Gibbs Memorial Laboratory at Harvard University. pp. 360, Cambridge, Mass. Harvard University Press. Price, $2.00.

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The publishers and the editor are to be thanked for having made more accessible, "the thoughtful and suggestive writings of one of America's pioneers in the new physical chemistry." ARTHUR B. LAMB.

Rays of Positive Electricity and Their Application to Chemical Analysis. By SIR J. J. THOMSON, O.M., F.R.S., Pp.vii + 132 + 5 plates. Longmans Green and Company. London and New York. Price 5 S., net.

A book written by Sir J. J. Thomson describing his researches is always in demand, and chemists and physicists generally will welcome this account of his latest triumph. The book deals with "the experiments on positive rays which have been made at the Cavendish Laboratory during the last seven years," and includes, in addition, short accounts of Gehrcke and Reichenheim's experiments on anode rays, also the researches of Stark and others on the Doppler effect in positive rays, amplifying and interpreting these by means of his own work on positive rays. Short chapters are included on spectra produced by bombardment with, and the disintegration of metals under the action of, positive rays. It concludes with an extended chapter on the use of positive rays for chemical analysis, giving, as illustrations of the method, accounts of his own researches on the "element of atomic weight 22," on the nature of X_3 the substance giving the "3" line, and on the evolution of helium and neon.

It should be noted that the choice of words is characteristic of the author. The name "positive rays" is used in preference to "canal rays" as originally applied by Goldstein. The heavy carriers are designated as "particles" instead of "ions," and the word "corpuscle" is retained for what is generally termed an electron.

The opening chapter includes a brief statement of the theory that obtains for the magnetic and electrostatic deflections of a carrier. This is followed by a detailed description of the author's experiments made in 1906. A number of improvements, in both design and manipulation soon suggested themselves, and in 1910 the author began the use of the photographic plate placed inside of the exhausted vessel for obtaining a permanent record of the deflection of the rays. Under the simultaneous action, at right angles to each other, of the electrostatic and magnetic fields, the trace on the photographic plate becomes a parabola. By increasing the strength of the fields the parabolas may be given any position on the plate desired; if, however, the fields are kept constant the positions of the parabolas depend directly on the masses of the carriers, and, since the mass bears a simple relation to the atomic weight, the nature of the particles can be identified.

Numerous photographs are reproduced. These are accompanied by detailed discussions. During the course of the investigation it was found that these carriers may, in the case of many substances, hold more than one charge. This introduces difficulties of measurement and of interpretation, that, but for the wonderful experimental skill and scientific imagination of the author, coupled with mathematical insight, might lead to wrong conclusions. As an example, in explaining why certain lines were of exceptional brightness on the photographic plate, the author says, "the view which seems to accord best with the observations is that the negatively electrified atoms are atoms which were positively electrified when in the discharge tube, that they got neutralized after passing through the cathode by combining with a corpuscle, and in this neutral condition exerted so strong an attraction upon a corpuscle that they were able to capture it though moving past it with an exceedingly high velocity."

Though the photographic plate furnishes an excellent means of detecting the existence of positively charged particles of different kinds it is not suitable for comparing the number of these particles present in a bundle of positive rays. The effect upon the photographic plate is determined largely by the depth to which the particles penetrate into the film. The light hydrogen atoms having a velocity of about fourteen times that of the heavy mercury atoms penetrate the film farther and therefore produce a greater photographic effect. Hence the intensity of the parabolic line is by no means proportional to the amount of the element present producing it. As an example the hydrogen line is always very intense, yet there may be relatively very little hydrogen present. To show this to be the case the author used an ingenious device which enabled the total charge carried by the particles forming the parabola to be collected on an electrometer, and thus the number of charged particles was estimated.

Next follows a chapter on the information afforded by the positive rays as to the constitution of a gas, the nature and properties of the molecules, and the process of ionization in a discharge tube. Short chapters are given to a consideration of retrograde and anode rays, followed by Stark's observations on the Doppler effect and amplified by the author's own researches.

The chapter on the use of positive rays for chemical analysis is very suggestive. The method is a new departure in chemical analysis and is very powerful. (*a*) Only a small quantity of gas is required—less than 0.01 cc. at atmospheric pressure will give well defined parabolas. (*b*) A new gas in the tube is indicated by a corresponding new parabola, and from its position on the plate its atomic weight may be determined. The method is more sensitive than that of spectrum analysis. The author's claim that "the technique is not difficult if appliances for producing high vacua are available" may be challenged by some attempting this method of chemical analysis. To produce and maintain for hours at a time a vacuum of 0.001 mm. mercury in a discharge vessel the construction of which of necessity requires the use of numerous waxed joints, in itself requires superior skill. To this add the manipulative skill attending the various details of operation such as proportioning the strength of the deflecting fields, giving the proper time of exposure, and finally determining the constants of the apparatus, gives a fair idea of the technique required for the successful use of the method. The success of the method at the Cavendish laboratory is a compliment to the wonderful experimental skill of the author and those assisting him. The method marks a great advance in modern chemical analysis.

As an application of the method he gives Mr. Aston's interesting investigation of neon. A number of photographs taken with the lighter constituents show lines corresponding to helium, to neon, to argon, and an additional line corresponding to an element with an atomic weight 22. The atomic weight of neon is 20.2. The evidence brought out by this method seems to point to a new element of atomic weight 22.

The book concludes with a consideration of the continuous evolution of helium and neon when various substances are bombarded by cathode rays. The gases were examined by the positive ray method. The author does not draw any very definite conclusions from his experiments. He says, "The view that helium can be got from other chemical elements raises questions of such fundamental character that few will be prepared to accept it until every other explanation has been found to be untenable," and adds that further "experiments are being made with this object but there are very considerable difficulties to be overcome."

CHAS. T. KNIPP.

Physikalische Chemie der homogenen und heterogenen Gasreaktionen unter besonder Berücksichtigung der Strahlungs- und Quanten-lehre sowie des Nernstschen Theorems. DR. KARL JELLINEK, Privatdozent an der Kgl. Technischen Hochschule, Danzig. S. Hirzel, Leipsig, 1913. 814 pp. 221 figures and 104 tables. Price, 32 marks.

For the reader, inclined perhaps to expect in this volume merely a more extended treatment of the themes usually comprised under the statics and kinetics of gas reactions, there awaits a complete surprise.

As the author states in his introduction, he would date the beginning of a new period in the development of physical chemistry from the announcement of Planck's quantum theory (1900) and of Nernst's heat theorem (1906). These two principles in conjunction with the laws of electronics and of energy radiation, he believes are destined to direct the future advancement of some of the most important branches of physical chemistry. It is for this reason that he has sought to incorporate these principles into the science as fundamental in the correct interpretation of the phenomena of gas reactions.

The task which the author has set himself, to review an old and much investigated field from entirely new theoretical standpoints, and to attempt, at this initial period, to weld the theories and the experimental results into a consequential whole, constitutes an ambitious program. One can but admire the skill the author has shown in attacking his problem and the success that he has met, for the most part, in its solution. If portions of the subject here and there appear incomplete or not entirely definite, the charge should be laid against the present undeveloped status of some of the subjects touched on, rather than the author's treatment. That his plan as outlined has been faithfully adhered to, is evidenced in the fact that little more than one-third of the text is given up to chemical statics and dynamics in the ordinary sense, the rest being devoted, either to the development of the necessary physical theories, or to their application to the phenomena of gas reactions. If the author has succeeded in one thing more than another, it should be in impressing on the reader the ever increasing necessity of the physical chemist following closely the physicist into many of his newest realms of investigation, or sometimes taking the lead, as has been illustrated by Nernst's development of his heat theorem.

The statics of gas reactions is subdivided in the first 700 pp. into theoretical and experimental parts, under the former of which are treated: the two laws of thermodynamics; the application of reversible cycles to homogeneous and heterogeneous equilibria; the statics of gas reactions treated by the aid of the conception of entropy, and the related concepts of free energy and thermodynamic potential, in which connection, the relation of Nernst's theorem to entropy, and entropy from the static-kinetic standpoint are developed at length. Further as belonging to statics, the laws of heat radiation are dealt with under sections on. (*a*) Fundamentals of the theory of heat radiation; (1) phenomena at the interior of a radiating medium, (2) phenomena dependent on the surface properties of the radiator; (*b*) Kirchoff's law; (*c*) radiation pressure; (*d*) Stefan-Boltzmann law of radiation; (*e*) Wien's law of displacement; (*f*) entropy and temperature of a uniform bundle of rays of definite frequency; (*h*) Planck's radiation formula, including the development of the quantum theory. The final section of the theoretical discussion of gas kinetics is particularly instructive and worthy of commendation for its exposition of the relation between the theory of heat radiation and specific heat, heat of reaction, temperature and Nernst's heat theorem.

To the *experimental* part of gas statics about 200 pp. are devoted, the same general order of subject matter being followed as in the foregoing sections on theory. The subjects treated are: I. Experiments in heat radiation; II. Determination of molecular vibration frequencies with the aid of radiation methods; III. Measurement of temperature; IV. Measurement of specific heat and heat of reaction, dealing especially with the recent work of Nernst and his school; V. Determination of gas equilibria experimentally.

The kinetics of gas reactions receive a somewhat meagre treatment, comprised in about 35 pp. which may be perhaps understood, in view of the author's standpoint and the fact that this field has not hitherto lent itself so readily to interpretation in the light of the new theories as has that of gas statics. But in a text devoting itself to the physical chemistry of gas reactions, this brevity must appear, from the standpoint of Guldberg and Waage's law, difficult to justify; on the other hand, one should welcome the fact that the space thus saved has been utilized in the consideration of other less well appreciated themes.

In the two final sections of about 50 pp. each, the author deals with the electrochemistry and the photochemistry of gas reactions. Under the former are described some interesting experiments in the production of chemical action by various forms of radiant energy capable of producing ionization in the gases acted on, and some very suggestive viewpoints are presented as to the electrical nature of these gas reactions. The reviewer has already had occasion to call attention in this connection to the neglect of the *radioactive* agencies (*Z. physik. Chem.*, **84**, 759).

Finally one finds much pleasure in the full references to the literature and the splendid indexes. A feature well worthy of mention is, that besides a complete *subject index*, the subjects are also repeated together with the page reference in the *authors' index*, which proves a very time saving device for the reader, and one highly to be recommended.

S. C. LIND.

Molécules, Atomes et Notations Chimiques. Memoirs of Gay-Lussac, Avogadro, Ampère, Dumas, Gaudin and Gerhardt. Vol. IV of Les Classiques de la Science. One plate, pp. 116. Librairie Armand Colin, Paris, 1913. Price, 1 fr. 20.

This volume contains the memoirs of Gay-Lussac on the combination of gases; of Avogadro on the relative masses of the molecules; of Ampère on combining proportions; of Dumas on the atomic theory and on chemical notation; of Gaudin on the structure of inorganic substances; and of Gerhardt on chemical formulas.

The memoirs are arranged to show the gradual development of our ideas of the atom and the molecule. To this end H. Le Chatelier, the editor of this volume, has added the modern equivalents wherever an obsolete or mistaken nomenclature has been used by the author, and has also inserted a number of explanatory notes showing the historical or logical sequence of the separate contributions.

The contents of this volume show in striking fashion the predominant position of France in the scientific world of the first half of the nineteenth century, and at least make us charitable toward the famous pronouncement of Wurtz in 1868 that "Chemistry is a French science." Nevertheless, it is unfortunate that to-day, in a collection such as this, there could not have been a fuller recognition of the contributions toward the solution of these fundamental problems which have been made outside of France. ARTHUR B. LAMB.

L'Air, L'Acide Carbonique et L'Eau. Memoirs of Dumas, Stas and Boussingault Vol. I, of Les Classiques de la Science. 4 plates and an engraving. pp. 104. Librairie Armand Colin, Paris, 1913. Price, 1 fr. 30.

This volume contains the classic memoirs of Dumas and Boussingault on the composition of atmospheric air; those of Dumas and Stas, and of Stas, on the atomic weight of carbon; and that of Dumas on the composition of water. There are also biographical notes by H. Le Chatelier on Dumas, and by H. Gautier on Boussingault and Stas.

This volume and the others of the series appear to be carefully prepared. They will be welcomed, not only by the specialist in the history of chemistry, but by a wider circle of readers who find enjoyment and inspiration in observing the skill, acumen and preseverance with which these early investigators attacked their fundamental problems. The biographical notes of Gautier and of Le Chatelier are, of course, good. They are especially useful in giving the French, in contradistinction to the more familiar, German point of view. ARTHUR B. LAMB.

Die Atome. VON JEAN PERRIN, Professor an der Sorbonne, Paris. Mit Autorization des Verfassers deutsch herausgegeben, von DR. A. LOTTERMOSER, A. O. Professor an der Königlich Technischen Hochschule, Dresden. Mit dreizehn Abbildungen im Text. pp. XV. + 196. Theodor Steinkopff. Dresden and Leipzig. 1914. Price, M. 5, paper; M. 6, cloth.

The extent and nature of the field covered in this monograph is shown by the following list of chapter headings.

I. Atom theory and chemistry: molecules; atoms; the hypothesis of Avogadro; structure of molecules; solutions; the upper limit of molecular magnitudes.

II. Molecular motion: molecular velocity; molecular rotation and vibration; mean free path.

III. The Brownian movement: emulsions; history and general characteristics; statistical equilibrium in emulsions.

IV. The laws of the Brownian movement: Einstein's theory; the results of experiment.

V. Fluctuations: Smoluchowski's theory.

VI. Radiant energy and quanta: the black body; extension of the quantum theory.

VII. The atom of electricity: ionization of gases; the atomistic structure of electricity.

VIII. The genesis and destruction of atoms: transmutation; counting the atoms.

The subject is treated in the exceedingly lucid and attractive style which characterizes all of the author's writings and which has been well preserved by the translator. On most of the topics discussed the author is an acknowledged authority, but in a few instances (as in the section in solutions, Chapter I) he is evidently not entirely at home and the subject is presented in a conventional manner and from a rather antiquated point of view, which contrasts strongly with the rest of the book. The ingenious speculations indulged in, in many instances, are nearly always interesting and highly suggestive, although in some cases (as in section 96) many readers will find it difficult to agree with the author's point of view. On the whole the book, is for the average reader, the most complete and best written treatment of modern atomistics which has yet been produced and is one which every teacher of any branch of chemistry ought to read.

E. W. WASHBURN.

Progressive Chemistry; Practical Experiments for Secondary Schools. By the Teachers of Chemistry in the High Schools of Minneapolis. MISS KATE MACDERMID, 2703 Bloomington Avenue, Minneapolis, Minn. Price, 35 cents.

This collection contains about 60 well selected and well arranged laboratory experiments, each one upon a perforated page. The authors have evidently had two objects in view: to select experiments which require only the simpler forms of apparatus; and to draw from common experience in such a way as to arouse interest in the chemistry of daily life. It is to be regretted that the "spoonful" is used as a measure of quantity and that there is not a more systematic treatment of the tests for the metals. As a whole, however, the collection is admirably suited to its purpose.

B. S. HOPKINS.

Notions fondamentales de Chimie organique. Par CHARLES MOUREAU, Membre de l'Institut et de l'Académie de Médecine, Professeur à l'École supérieure de Pharmacie de l'Université de Paris. Quartrième edition. Paris: Gauthier-Villars, 1913. 9 Fr. 383 pp.

Previous editions of this book have been reviewed in THIS JOURNAL.[1]

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[1] 32, 1362.

The present edition, which is the fourth, contains the more important of the recently discovered facts which should be considered in a book of small size. The order of arrangement of the several classes of compounds is the same as that used in earlier editions; it is severely logical according to the symbols of the elements present. This method often leads to unfortunate results if the student using the book is to be considered. For example, in the chapter on hydrocarbons, the first class of compounds described, the structure of naphthalene is deduced from the transformation of phenylisocrotonic acid into α-naphthol. Under alcohols, borneol and menthol are described, and their graphic formulas given without any statements as to the reasons for their structure or their relation to other compounds. The alphabetical arrangement leads to other curious results. In the chapter on amines, those containing one, two, and more nitrogen atoms are described. This leads to the consecutive treatment of putrescine, cadaverine, and rosaniline. The appearance of the fourth edition is evidence, however, that the book has found a place. It could be used profitably by a student, familiar with organic chemistry, in preparing for an examination, when it is desired to have many facts given in as brief space as possible. JAMES F. NORRIS.

The Application of Physico-Chemical Theory to Technical Processes and Manufacturing Methods. R. KREMANN. Translated from the German by H. E. POTTS and edited by ALBERT MOND D. Van Nostrand Co., New York 1913. 212 pp. Price, $3.00.

The author's preface says:

"Physical chemistry used to be considered a somewhat theoretical branch of study, but it has recently developed in such a way as to explain many of the empirical observations of technology and to prove extremely suggestive of many new methods. Such a tendency may be considered one of the highest aims of scientific research.

"The young chemist frequently feels this in his first few terms, and I have found that of all the problems of physical chemistry the beginner shows most interest in those which have a bearing on technical questions. On this account, for some years now I have devoted a special section of my main course on physical chemistry to 'the application of physico-chemical theories to technical problems.'"

The opening chapter discusses the laws of thermo-dynamics and derives the general equation for the free energy of reactions between gases, and discusses its application to several cases: gas engines, the production of producer gas and water gas and the Deacon process. The second and third chapters deal with reaction velocity, catalysis and chemical equilibrium and discuss numerous illustrations among which may be mentioned; the drying of linseed oil, devitrification, the chamber process and the contact process for sulfuric acid and the preparation by caustic soda from sodium carbonate. The last four chapters discuss about a score of industrial processes of a very varied nature from the standpoint of the phase rule, *e. g.*, the reactions in the iron blast furnaces, the alloys of iron and carbon, the ammonia-soda process, the setting of Portland cement, the manufacture of soap and many others.

Although colloidal solutions receive their share of attention the properties of true solutions are ignored. In the reviewer's opinion the book would be strengthened by a discussion of fractional distillation, of the multiple effect vacuum evaporator, and of the great technical significance of the latent heat of vaporization of water. Electrochemical processes and photochemical processes are omitted entirely.

Students who have had courses in both physical chemistry and industrial chemistry will be aided in making the connection between these branches of chemistry by a study of the book. The book deserves a place on the reference shelves of our college libraries. GRINNELL JONES.

Die Methoden der Massanalyse. VON DR. H. BECKURTS. Unter Mitwirkung VON DR. O LÜNING. pp. 843–1122. 1913. Braunschweig: F. Vieweg & Son. Price, 8 Marks.

This is the third part, comprising the precipitation methods, of the 8th edition of F. Mohr's Lehrbuch. The first edition of this classic of German chemistry was issued in 1855–56; the fourth edition in 1874 covered 774 pages. In the present edition we not only have an account of the methods added since the last edition appeared but also a dissertation on the theory of precipitation analysis, a brief history of precipitation analysis and, in an appendix, a history of volumetric analysis. From this last it appears that the earliest volumetric analysis is described by Dr. F. Home in a book printed in Edinburgh in 1756 which was translated into French in 1762. The German translation which was published at Leipzig in 1762 was entitled "Versuche im Bleichen." The method consisted in adding dilute nitric acid to a weighed amount of pearlash until effervescence ceased. The volume consumed gave a measure of the goodness of the ash.

EDWARD HART.

Practical Methods of Organic Chemistry. By LUDWIG GATTERMANN. Third English edition translated from the eleventh German edition by WILLIAM B. SCHOBER and VAHAN S. BABASINIAN. Macmillan & Co. New York. 1914. XVII—401 pp. Price, $1.75

More chemists have received their early organic laboratory training from Gattermann's laboratory manual than from any other similar book. This, together with the fact that the manual has lived through eleven German editions is ample evidence that there is something very vital about it. The well chosen, carefully tested directions for laboratory procedure, and the good theoretical discussions won the book a place in its early editions, and this place it has held up to the present. There is nothing which attests to the vital nature of the parent German book more than the use in many American schools of the imperfect English translation. The English book now enters upon its third edition from the eleventh German edition. Any teacher in intimate daily contact with students in the laboratory is familiar with the ambiguities of the text of the second edition. In spite of this, those of us who have called the attention of class after class to its uncertainties and errors have continued to use the book with the hope that a new edition would soon relieve us of the burden of explanation. The new edition has now come and it is more than a disappointment, it is a real shock to find that it is practically a reprint of the second edition with the new parts of the recent German editions added. Those of us who have grown up with Gattermann, have suffered with the imperfections of the English rendition, have issued typewritten sheets to supplement it, and yet with all this have continued to use it, had hoped for better treatment. Here was an opportunity for a translator and for a publisher to reward their old friends, and win new adherents by issuing a carefully prepared, completely revised and modernized English edition. As it is there is certainly good reason to doubt the power of the new edition to much longer hold the admirers of the old Gattermann. It would be a decided loss to organic chemistry in America to have this book fall behind and become valuable for historical reasons only, yet there is evidence that such will be the case unless there is a change in policy on the part of those in control of the book.

Not all the fault lies with the English edition. The recent German editions are marked by a conservatism not in harmony with the development of the last fifteen years. For example, what effective worker would prepare melting point tubes and take melting points as Gattermann directs? What modern laboratory would allow elementary students to distil ether over a water bath heated by a gas flame protected by a wire gauze, or would compel them to heat water, turn out their flames and then use the hot water? Electricity and steam as safe sources of heat are too common not to find mention in a modern book. In the matter of preparations ultra-conservatism is shown in retaining the old and omitting the new. Opinions may differ widely as to what preparations should be omitted, but there can be no question that some new ones should be added. For example, hydrogenization under the influence of metallic nickel, colloidal platinum or palladium has been so simplified that examples of it have been included in recently published manuals (Noyes, Henle, Dupont, Freundler and Marquis) but the reaction is not found in Gattermann. The same is true of the use of finely divided metallic copper as a catalyst in a host of reactions suitable for elementary students. There is not a single preparation in Gattermann involving the use of the electric current even in so well known a reaction as the reduction of nitro compounds (cf. Ullmann, Noyes, Henle, Sudborough and James). The preparation of triphenylchloromethane and its conversion into triphenylmethyl and its peroxide are so simple that they have found a place in the newer laboratory manuals (Noyes and Henle), but not in Gattermann. The introduction into the new English edition of a few changes of the type just mentioned would have made the book much more satisfactory. Failing in this, it might at least have been freed from those ambiguities which so disfigured the old edition. For example, "a solution of 10 g. of aniline in 50 g. of water is previously prepared according to the directions already given, and exactly the theoretical amount of hydrochloric acid, after it has been well cooled with ice water, is added to the diazo solution, with stirring" page, 262. "On account of the splendid phenomena, steam should be passed into the oxidation liquid " page 224. "The melted mass is then poured on a strong copper plate the edges of which have been turned up and of sufficient size so " page 294. Many more such examples could be quoted.

In spite of all this many of us will continue to use Gattermann in our classes, especially the German edition in so far as our students are able to read it. We will increase the number of supplementary directions given, and will continue to hope that the next English edition will be more clearly written and will include a more progressive list of preparations.

This third English edition is an attempt to reproduce the eleventh German edition. The German edition has been in print for two years and is familiar to most teachers of organic chemistry. It is essentially the same book as the tenth edition which differed from the ninth edition only by the addition of a description of Dennstedt's rapid method of combustion. Two examples of the Barbier-Grignard reaction which have been in the German since the sixth edition, issued in 1903, and a theoretical discussion of steam distillation, extraction, etc., which have been in the German since 1905 appear now for the first time in the English translation.

L. H. CONE.

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[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No 233]

THE EXTENSION OF THE DILUTION LAW TO CONCENTRATED SOLUTIONS.

BY JAMES KENDALL

Received January 23, 1914

The dilution law of Ostwald:

$$\gamma^2/(1 - \gamma).v = K; \quad \text{or} \quad c_i^2/c_u = K, \qquad (1)$$

(γ = fraction ionized, v = dilution, c_i = ionic concentration, c_u = concentration of un-ionized part, K = dissociation constant), is apparently securely based upon the principle of mass action, and yet has definite limits in its *exact* applicability to aqueous solutions of electrolytes. The law is found, on examination,[1] to break down in two directions.

In the first place, it is followed exactly only if the *ionic concentration* is small. When a certain limiting ionic concentration (approximately 0.01 N) is exceeded, K begins to increase, and increases steadily with c_i. Divergences from the dilution law in this direction are, therefore, met with in all strong electrolytes, and also in many of the transition electrolytes[2] at the higher concentrations. (Anomaly of strong electrolytes.)

In the second place, the law is followed exactly only if the *total concentration* of the electrolyte is small. The limit of exact applicability is fixed by Wegscheider[1] as lying between $v = 32$ and $v = 16$, for typical weak electrolytes. In more concentrated solutions K shows a *decreasing* value, and the decrease becomes more and more rapid with increase of concentration. (Anomaly of concentrated solutions.) It is usual to connect this decrease with the increased viscosity of these concentrated solutions.

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[1] Wegscheider, *Z. physik. Chem*., **69**, 603 (1909).

[2] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

In concentrated solutions of strong and transition electrolytes, both disturbing influences are present and will partially counterbalance one another. Such cases have been investigated in a previous communication,[2] where it is shown that the ionic concentration influence is more important in relatively dilute solutions, and the total concentration influence in more concentrated solutions. A maximum value for K is thus observed at a certain concentration, the exact point being dependent upon the strength of the electrolyte.

It will be evident that the limits stated above for the exact applicability of the dilution law are only approximate. More exact experimental determinations will establish divergences in solutions still more dilute.[3]

The partial failure of the dilution law has led to the proposal of many alternative formulae for the expression of the dissociation equilibrium. Empirical equations for strong electrolytes have been put forward, among many others, by Rudolphi,[4] van't Hoff,[5] and Storch.[6] None of these is exactly applicable in all cases, and none has been shown to possess a definite theoretical basis. Similarly, no satisfactory formula has been found to apply to all concentrated solutions.

Recently, a number of formulae of a more general type have been proposed, expressing in one equation the dissociation equilibrium of all electrolytes. Such are the equations of Kraus and Bray,[7] and of MacDougall,[8] which are intermediate between the dilution law and Storch's equation, and may be written in the form:

$$c_i^2/c_u = K + D.c_i^n \qquad (2)$$

(K, D and n are constants varying with the electrolyte.) Simultaneously, the present author[9] put forward a similar equation:

$$\gamma^2/(1-\gamma)v = K + c.(1-\gamma)/\gamma \qquad (3)$$

(K and c are constants varying with the electrolyte.) This equation is intermediate between the dilution law and van't Hoff's formula, and is less general than equation (2) only because of the absence of a third variable constant. The equation represents satisfactorily the dissociation equilibrium of acids *of all strengths* in aqueous solutions of lower concentration than $v = 16$.

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[1] *Loc. cit.*

[2] Kendall, *Meddel. från K. Vet. Akads. Nobelinstitut*, Band 2, No. 38 (1913).

[3] Kendall, *J. Chem. Soc.*, 101, 1288 (1912).

[4] Rudolphi, *Z. physik. Chem.*, 17, 385 (1895).

[5] Van't Hoff, *Ibid.*, 18, 300 (1895).

[6] Storch, *Ibid.*, 19, 13 (1896).

[7] Kraus and Bray, This Journal, 35, 1315 (1913).

[8] MacDougall, *Ibid.*, 34, 855 (1912).

[9] Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

In a second communication,[1] more concentrated solutions of acids of widely divergent strengths have been examined. Here equation (3) fails to apply, and gives—just as does the dilution law for weak electrolytes—values greater than the experimental value for $\gamma^2/(1 - \gamma)v$. The present paper continues the investigation of these concentrated solutions. For simplicity, typical weak electrolytes are first considered. Here it is possible to deal with the "anomaly of concentrated solutions" alone, since c_i is always exceedingly small. Subsequently, the transition electrolytes are briefly examined; the case of strong electrolytes is reserved for a future communication.

The Ostwald dilution law, as it stands, fails to represent accurately the dissociation equilibrium of *concentrated* solutions of a weak electrolyte. This failure, however, is easy to comprehend, since from thermodynamical considerations it is evident that the law can apply *exactly* only to dilute solutions, and must, of necessity, break down when the concentration of the solute is increased beyond certain limits. In the following pages a modified form of the dilution law is deduced, which is found to be exactly applicable even at high concentrations, and a possible theoretical basis for this modified law is indicated. It is then shown that, with the assumption of this theoretical basis, a thermodynamic investigation leads to the result that the modified law, unlike the original dilution law, would indeed hold exactly at all concentrations. Its agreement with the experimental data at high concentrations is demonstrated for several typical weak electrolytes, and its applicability to equation (3) for transition electrolytes is exemplified. Finally, the arguments in favor of the theoretical conclusions drawn are summarized.

The Anomaly of Concentrated Solutions.—A good illustration of the decrease in the dissociation constant of a weak electrolyte at high concentrations is given by the figures for acetic acid in Tables I and II, below.

TABLE I.—ACETIC ACID, 25° (KENDALL).

v	Λ	100 K	η.	100 K_1.	d.	100 K_2
0.989	1.443	0.00140	1.112	0.00174	1.0084	0.00184
1.977	2.211	0.00165	1.056	0.00183	1.0043	0.00188
3.954	3.221	0.00176	1.028	0.00186	1.0022	0.00188
7.908	4.618	0.00181	1.014	0.00187	1.0011	0.00188
15.816	6.561	0.00184	1.007	0.00187	1.0006	0.00187
31.63	9.260	0.00185	1.003	0.00186	1.0003	0.00186
63.26	13.03	0.00185	1.002	0.00186	1.0002	0.00186
∞	387.9	.....	..	..	...	...

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[1] Kendall, *Meddel från K. Vet. Akads. Nobelinstitut*, Band 2, No. 38 (1913).

TABLE II.—ACETIC ACID, 25° (RIVETT AND SIDGWICK).

$1/v$.	Λ/v.	$100\,K$.	η.	$100\,K_1$.	d.	$100\,K_2$.
2.9771	1.854	0.00077	1.347	0.00139	1.0235	0.00165
2.0060	1.789	0.00106	1.230	0.00161	1.0162	0.00180
1.4886	1.671	0.00125	1.169	0.00172	1.0122	0.00186
1.3374	1.620	0.00131	1.150	0.00173	1.0109	0.00186
1.0029	1.474	0.00144	1.112	0.00179	1.0084	0.00189
0.8917	1.415	0.00150	1.098	0.00181	1.0074	0.00190
0.6687	1.264	0.00160	1.073	0.00184	1.0036	0.00191
0.3722	0.9722	0.00170	1.041	0.00184	1.0032	0.00188
0.1861	0.7079	0.00181	1.021	0.00188	1.0017	0.00190
0.0930	0.4986	0.00180	1.010	0.00184	1.0009	(0.00185)
0.0402	0.3372	0.00192	1.004	0.00195	1.0004	(0.00195)

The experimental data in Table II are selected from a series of determinations by Rivett and Sidgwick;[1] the density and viscosity results in both tables are also obtained from the same paper, by interpolation from the figures there given. (Λ = equivalent conductivity, η = relative viscosity (water unity), d = relative density.)

It will be seen, from the third column of these tables, that the dissociation constant $100\,K$ is a true constant for solutions less concentrated than $v = 16$, but that for higher concentrations the value obtained decreases, first slowly and afterwards more rapidly. (In Table II the constancy of the values at high dilutions is rather obscured by the relatively greater experimental error.)

There is, however, a viscosity correction to be applied to these results. The exact relation between conductivity and viscosity has been investigated and established by the researches of Green,[2] Johnston,[3] Washburn,[4] and Noyes and Falk.[5] The general conclusion drawn is that the simple equation,

$$\Lambda\eta/\Lambda_0\eta_0 = \text{constant}, \qquad (4)$$

(Λ_0 = equivalent conductivity and η_0 = viscosity at zero concentration of solute) is not exactly followed; but rather the equation,

$$\Lambda/\Lambda_0 = \text{constant}\ (\eta_0/\eta)^n, \qquad (5)$$

(n is a constant varying with the electrolyte.) Nevertheless, n is in most cases so nearly equal to unity, and its exact determination is a matter of such difficulty, that we may assume, with Noyes, that the safest correction we can make is by the use of equation (4) above. In any case, the residual error will be small, unless very high concentrations (above normal) are considered.

Hence we obtain the corrected values for the dissociation constant by employing the expression $\Lambda\eta$ instead of the experimental value Λ for the equivalent conductivity in the above tables. These corrected values are given under the heading $100\,K_1$. The application of the viscosity correction has not destroyed the divergences at the highest concentrations, where a steady decrease in the dissociation constant is still evident. Further examination into the cause of these divergences is therefore necessary.

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[1] Rivett and Sidgwick, *J. Chem. Soc.*, 97, 734 (1910).

[2] Green, *J. Chem. Soc.*, 93, 2049 (1908).

[3] Johnston, THIS JOURNAL, 31, 1010 (1909).

[4] Washburn, *Ibid.*, 33, 1461 (1911).

[5] Noyes and Falk, *Ibid.*, 34, 454 (1912).

In the following section, the dilution law itself is critically examined and its exact theoretical basis tested. A modified form of the dilution law is tentatively proposed, which is subsequently applied to the above experimental data and found to account for the divergences up to very high concentrations.

A Modification of the Dilution Law.—The exact significance of the Ostwald dilution law will first be studied from the simple kinetic standpoint.

We have, for a uni-univalent electrolyte of the type RX, the dissociation equation,

$$\mathrm{RX} \rightleftharpoons \mathrm{R}^+ + \mathrm{X}^-, \qquad (6)$$

from which, by the application of the law of mass action, the dilution law is immediately obtained in the form

$$c_i^2/c_u = K. \qquad (7)$$

The right-hand side of equation (6) presents no difficulty from the kinetic standpoint.[1] The concentration of each ion is c_i, and by the impact of two ions of opposite charge the undissociated salt is formed, with the mutual neutralization of the charges. The mechanism of the equilibrium reaction on the other side of the equation, however, is by no means so clear. *A definite conception of the nature of the reaction on the left-hand side of the equation has not yet been obtained, and, in spite of the importance of the question, it does not seem to have attracted any great attention, or to have been answered in any but the vaguest manner.*

The above statement may be further emphasized by an extract from a recent communication by Walden:[2] "The greater the dielectric constant of the interposed solvent, the less is the electrostatic attractive force [between ions of unlike charge], and with the greater difficulty does the recombination to electrically neutral molecules take place. Nevertheless, the neutral molecules will be formed in the solution. Why then do they again break up into ions? *For what reason does the neutral salt molecule break up into ions at all, as soon as it enters into solution?* This fundamental question has, up to the present, not been answered. Strangely enough, we do not even make a serious attempt at its solution."

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[1] That is, so long as the ionic concentration is small. If c_i exceed a certain limit, then the electrostatic forces existing between the charged ions become of importance in the equilibrium, and we have the "anomaly of strong electrolytes"

[2] Walden, THIS JOURNAL, 35, 1649 (1913). This communication first reached the author's notice after the present investigation was practically completed. Walden has attacked the subject from precisely the opposite direction to that here followed, namely, by a consideration of the "anomaly of strong electrolytes" from the increase in the dielectric constant of the solvent due to the dissolved salt. The view is expressed that "the process of disaggregation of the polymerized salt molecules also causes and induces the process of ionic cleavage." The conclusions drawn in the present paper are not necessarily in opposition to those advanced by Walden, but may rather be considered as confirming and supplementing them, as will be shown later.

In the dilution law, as it stands, it is tacitly assumed that the undissociated molecules RX break up *quite spontaneously* into the separate ions R^+ and X^-. The whole equilibrium is taken to be exactly analogous to that existing in gaseous dissociation, and the analogy is indeed sufficiently striking. Nevertheless, there are fundamental differences between the two phenomena of gaseous and ionic dissociation, and one is the influence of the solvent medium upon the equilibrium in the latter case. *The nature of the solvent plays an important part in determining the degree of dissociation of the dissolved electrolyte.*

The role of the solvent in the dissociation equilibrium (except from the point of view of the dielectric constant) has been strangely neglected by the followers of the dissociation theory of Arrhenius.[1] The tendency has been to treat the solvent simply as so much "dead space." The upholders of the solvate theory, on the other hand, have referred all dissociation phenomena to interaction between solvent and solute.

A general, but indefinite, feeling of dissatisfaction with the present position (as is indicated above by Walden) has certainly existed among the followers of the dissociation theory, and this feeling has occasionally found its way into print in well-known text-books, where definitions of electrolytic dissociation may be found, which undoubtedly do not agree with the hypothesis of spontaneous dissociation of the undissociated molecule tacitly assumed above. For example, Stieglitz[2] states: "When an ionogen is dissolved in water, its molecules are immediately, more or less completely, *dissociated by the water* into smaller fragments or molecules of unlike composition." Similarly, Alexander Smith[3] writes: "The conducting power of the solution is indissolubly connected with the fact that the original molecules of the solute have been broken up by the solvent into smaller molecules containing one or more atoms." Nernst[4] states: "Der Umstand, dass gerade das Wasser die ganz besondere Fähigkeit besitzt, gelözte Stoffe electrolytisch zu spalten, legt die Vermutung nahe, dass bei der Ionenspaltung chemische Verbindungen mit dem Wasser eine Rolle spielen." Here there is not only the statement that *the solvent* splits up the undissociated molecules into the separate ions, but the possibility also is noted that, in so doing, the solvent actually combines with the solute to form hydrates and hydrated ions.[1] Ostwald[2] himself goes so far as to say: "Das Wasser nimmt, in Bezug auf seine Fähigkeit elektrolytische Lösungen zu bilden, oder Stoffe in Ionen zu spalten, eine ausgezeichnete Stellung ein." Arrhenius[3] also speaks of "die Fähigkeit der Lösungsmittel, Elektrolyte in Ionen zu zerlegen."

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[1] Compare Lowry, *Science Progress* (1908).

[2] Stieglitz, "Qualitative Chemical Analysis," Part I, page 41. The italics are in the original. See also pages 61–66, where the ionizing power of solvents (as related to their dielectric behavior, the unsaturated condition of their simple molecules, and their power of association) is critically examined, and the above idea is repeatedly expressed.

[3] Alexander Smith, "Introduction to Inorganic Chemistry," page 317.

[4] Nernst, *Theoretische Chemie, Sechste Auflage* (1909), page 534. See also repeated statements on pages 378–80.

Now, if the molecules of the undissociated salt in the solution are indeed broken up *by the molecules of the solvent* into the separate ions, then the concentration of the solvent in the solution should appear in the equation of equilibrium, and the simple dilution law is not valid. The equation is modified into the form:

$$c_i^2/c_u.c_s = K, \qquad (7)$$

(c_s = concentration of solvent in the solution.) At moderately high dilutions c_s becomes practically constant, and the equation reduces to the simple dilution law. At higher concentrations of solute, c_s begins to diminish, since molecules of solvent are being replaced in the solution by molecules of solute.

We may write equation (7) in the form:

$$c_i^2/c_u = Kc_s,$$

from which it is at once evident that the equation is *qualitatively* in accordance with the fact, shown by the results of experiment, that c_i^2/c_u is not constant at high concentration of solute, but exhibits a *decreasing* value. The validity of the equation at high concentrations may be tested *quantitatively* with the help of the density data.

This is done for acetic acid in the last columns of Tables I and II above. The values under 100 K are corrected by means of the ratio:

weight of solvent in one liter of pure solvent/weight of solvent in one liter of solution

and the results are given under 100 K_2, which therefore represents 100 K in equation (7) above.

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[1] The subject of the hydration of ions has recently attracted much attention; for a summary of the bearing of the subject on the present discussion see Wegscheider, *Z. physik. Chem.*, 69, 605–6 (1909). Ciamician, reviewing the results obtained, makes the significant statement: "Alles scheint darauf hinzuweisen dass die Annahme, nach welcher die Dissociation in Lösungen durch das Lösungsmittel vermittelt und bedingt wird, heute an Berechtigung gewonnen hat und den bekannten Tatsachen am besten entspricht," *Z. physik. Chem.*, 69, 100 (1909).

[2] Ostwald, *Lehrbuch der Allgemeinen Chemie*, Band 2, Teil 1 (1893), page 705.

[3] Arrhenius, *Lehrbuch der Elektrochemie* (1901), page 55. Also "Theories of Chemistry" (1907), page 83.

It will be seen that the values for the dissociation constant are now *really constant*, up to concentrations of solute well above normal. (In very highly concentrated solutions there is still a slight decrease; this is considered in a later section.) Equation (7) is therefore valid for the expression of the dissociation constant of acetic acid *in concentrated solutions*. In subsequent tables it is shown that it is similarly applicable to other weak electrolytes. Meanwhile, some theoretical consequences of the hypothesis put forward above will be considered and its legitimacy tested.

In one respect it will, at first sight, appear that the dilution law of Ostwald claims preference over the modified law advanced above, namely in its simplicity. In equation (7) a variable factor, c_s, has been brought into the equation for the dissociation equilibrium, and this factor varies with the concentration in the desired direction for improving the constancy of K' at high concentrations. Hence it may seem that the introduction of the variable factor c_s into the equation is simply a mathematical trick, which improves the agreement with the experimental results only by destroying the original simplicity of the dilution law. If this were indeed so, then the generally accepted theoretical basis lying behind the dilution law of Ostwald (the assumption of spontaneous dissociation of the undissociated molecule) could not legitimately be called into question here.

In the following section, however, it will be demonstrated that the above objection is not valid. The equilibrium of ionic dissociation has, so far, been considered only from the simple kinetic standpoint. When an exact thermodynamic examination is made, it is found that the original simplicity of the dilution law is not sacrificed by the modified view taken of the nature of the dissociation equilibrium; but that the dilution law has, on the other hand, *actually become less complicated*, inasmuch as certain simplifying assumptions, necessary for the development of the equation in its original form, may now be dispensed with.

Thermodynamic Investigation of the Dissociation Equilibrium.—The dilution law is first developed below in its original form and examined from the thermodynamic view-point. The modified form of the law, as deduced from the theoretical considerations advanced above, is then similarly derived, and the results compared.

For the Ostwald dilution law, the line of argument followed is substantially that given by Partington[1] in an investigation on the ionic equilibrium in solutions of electrolytes.

"The thermodynamic investigations lead to the equilibrium isotherm:[2]

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[1] Partington, *J. Chem. Soc.*, 97, 1159 (1910).

[2] It has been pointed out to the author by D. A. MacInnes that this is not a *purely* thermodynamic equation. From the laws of thermodynamics alone we arrive at the

$$n' \log c' + n'' \log c'' + n''' \log c''' + \dots\dots = \log K,$$

where K is a function of the temperature and total pressure for given components, but is constant at constant temperature and pressure. K is independent of the molecular concentration (c) and numbers of molecular weights (n) of the components. Thus:

$$c'^{n'}.c''^{n''}.c'''^{n'''} \dots\dots = K \qquad \text{(A)}$$

For the ionization of a binary electrolyte:

$$\underset{(c_u)}{\mathrm{RX}} \rightleftharpoons \underset{(c_i)}{\mathrm{R}^+} + \underset{(c_i)}{\mathrm{X}^-}$$

$$c_u/c_i^2 = K \qquad \text{(B)}$$

If n_u, n_i, n_i are the corresponding numbers of molecular weights of the components,

$$c_u = n_u/(n_u + 2n_i + n_s);$$

$$c_i = n_i/(n_u + 2n_i + n_s);$$

where n_s refers to the solvent.

Substituting in (B), we obtain:

$$n_u(n_u + 2n_i + n_s)/n_i^2 = \text{constant} \qquad \text{(C)}$$

This reduces, *when n_u and n_i are small compared with n_s*, to the form:

$$n_u.n_s/n_i^2 = \text{constant}$$

Let v be the volume of solution containing one molecular weight of total salt, then (*again only if n_u and n_i are small compared with n_s*), we have,

$$n_s = kv(n_u + n_i),$$

where k is a constant of proportionality.

Thus finally,

$$n_u(n_u + n_i)v/n_i^2 = \text{constant}. \qquad \text{(D)}$$

This equation is as far as thermodynamic theory will proceed; to bring the result into a region accessible to experimental test, a further assumption is necessary. The determination of n_i, the ionic concentration, is made possible if we accept Arrhenius' fundamental theorem that the ratio of the number of "active" (or ionized) molecules of the electrolyte to the total number, active and inactive, present in a given portion of solution is equal to the ratio of the molecular electrical conductivity of the solution to the limiting value of this when the dilution is very great:

$$n_i/(n_u + n_i) = \Lambda/\Lambda_0 = \gamma \qquad \text{(E)}$$

Substituting in (D) the value of $n_i/(n_u + n_i)$ from (E), we obtain:

$$\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)v = \text{constant} = K \qquad \text{(F)}$$

This is Ostwald's Dilution Law.

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equation: $n'v'd\pi' + n''v''d\pi'' + n'''v'''d\pi''' + \dots\dots = 0$. (Compare Washburn, THIS JOURNAL, 32, 484 (1910).) The equation given above is obtained by the integration of this and with the use of the further assumption that the relation $c = k\pi$ holds. (π = osmotic pressure, c = molecular concentration, k = constant.)

The thermodynamic derivation shows that the formula can, in any case, represent the course of ionization only in solutions of such dilution that the regions of solvent influenced by each molecule of solute are independent.

From the above argument it will be evident that the apparent simplicity of the Ostwald dilution law is obtained only at the sacrifice of its applicability to concentrated solutions. The changes necessary in the above thermodynamic derivation of the equation for the dissociation equilibrium, under the modified theoretical basis advanced above, may now be investigated.

The equation representing the process of ionization becomes:

$$RX + (H_2O) \rightleftharpoons R^+ + X^-,$$

corresponding with the view, expressed above, that the dissociation of the undissociated molecule RX into its component ions R^+ and X^- is brought about by impact with molecules of the solvent.

It may appear at this point that the above equation is incorrectly stated, inasmuch as it does not balance. As a matter of fact, the corresponding equation for the original dilution law also does not balance, since the ionic charges appear only on one side. It will be shown, in a subsequent section, that the solvent is not to be considered as acting *chemically* in the ionization equation written above. The process of dissociation is regarded as entirely *physical* in its nature, the action of the solvent molecules being ascribed to their unsaturated character, *i. e.*, to the free valences or "neutrons" attached to them. Thus the above equation is more correctly to be written:

$$RX + ⊕⊖ \rightleftharpoons R^+ + X^-,$$

where ⊕⊖ represents a neutron. This equation balances exactly. Since, however, the ionic charges are supplied directly by the molecules of the solvent, the concentration of the latter is the factor that must appear in the equation. The matter is discussed more fully later, in connection with the results of Walden.

From the above equation we obtain:

$$c_u . c_s / c_i^2 = K \tag{B'}$$

For c_s we have the relation:

$$c_s = n_s/(n_u + 2n_i + n_s),$$

c_u and c_i being transformed as before. We now obtain, in the next step, the equation:

$$n_u . n_s / n_i^2 = \text{constant}, \tag{C'}$$

which is *valid exactly at all concentrations.*

Let us now define v' as the number of *unit weights of solvent* employed to dissolve one equivalent weight of total salt. The change is thus made from volume concentration of the solute (equivalent weights per fixed volume of solution) to weight or molecular concentration (equivalent weights per fixed weight of solvent). Then we have:

$$n_s = k'v'(n_u + n_i),$$

where k' is a constant of proportionality.[1] This equation is also *exactly true for all concentrations.*

We now obtain:

$$n_u(n_u + n_i)v'/n_i^2 = \text{constant}, \qquad (\text{D}')$$

and finally, employing equation (E) as before, we have the modified dilution law,

$$\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda).v' = \text{constant} = K, \qquad (\text{F}')$$

both of which equations are valid not only for small concentrations of solute, but *for all concentrations.*

Equation (F′)—which is, of course, identical with the previous equation (7) above— therefore has, when compared with the dilution law in its original form, the two advantages of *simplicity* and of *agreement with the experimental data at high concentrations.* Several points in the above thermodynamic investigation, however, require more extended consideration; these are taken up in order below.

We have, first of all, the fact that it appears, on a first inspection of equation (F′) above, that there are two units of concentration simultaneously employed, namely in the expression of Λ (the equivalent conductivity, *i. e.*, the specific conductivity divided by the *volume concentration* of the solute) and of v' (the reciprocal of the *weight or molecular concentration* of the solute). However, the equation can be expressed, in terms of weight concentration only, without change of form, since Λ has the same value for either unit of concentration.

This becomes evident from an examination of the experimental method followed in the determination of equivalent conductivity. The quantity directly measured in experimental work is the specific electrical resistance of the solution. The specific conductivity, κ, is the reciprocal of this, and is proportional to the number of dissociated molecules in *unit volume of the solution.*[2] The equivalent conductivity Λ is equal to κv, where v represents the dilution in volume units.

If now, we change from volume concentration units to weight concentration units, thereby altering the dilution v to v', we must also modify our definition of specific conductivity, and this will now be proportional to the number of dissociated molecules in *unit weight of the solvent.* Consequently, if the specific conductivity under weight concentration units is κ', we have the relation:

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[1] k' represents the number of equivalent weights of the solvent contained in the fixed weight of solvent chosen as unit. The equation consequently represents both molecular and weight ratios between solute and solvent.

[2] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), pages 102–3.

$$\kappa' = \kappa.(v/v').$$

Hence the equivalent conductivity under weight units, $\kappa' v'$, is equal to κv. The equivalent conductivity Λ therefore has the same value, expressed in either unit of concentration.

A second point for examination is how far we are justified in considering the fundamental assumption of Arrhenius:

$$\Lambda/\Lambda_0 = \gamma, \text{ the degree of dissociation,}$$

as being applicable to concentrated solutions.

It is a much-debated question[1] whether this assumption is exactly true even at very high dilutions. In any case, it can be directly valid only if the ionic mobilities are not functions of the concentration. Now at high concentrations the ionic mobilities certainly are variable, since they are affected by the increased viscosity of the medium, and any correction (as for acetic acid in Tables I and II) can be only approximate. At high dilutions, however, the viscosity factor (that is, the change in the nature of the medium) may be neglected. Variation in ionic mobility at high dilutions, therefore, can occur only if mobility is a function of *ionic concentration*. That this is indeed the case was a view first advanced by Jahn,[2] in order to account for the "anomaly of strong electrolytes." Arrhenius,[3] however, showed that neither Jahn's theoretical work nor his experimental data were sufficiently reliable to warrant the conclusions drawn. The case of the hydrogen ion has been most frequently investigated, and here the majority of results[4] certainly point to the fact that the mobility is constant in dilute solutions.

The hypothesis of Jahn has recently been brought into prominence again by the work of Lewis.[5] The opposite view—that the ionic mobility is constant, and that the abnormality of strong electrolytes must be attributed to the change in the dissociating power of the solvent, due to the addition of solute—first advanced by Arrhenius,[6] has also been supported by the extended researches of Walden.[7]

Here a choice must be made between the two views, and since the assumption of varying ionic mobility in dilute solution must be regarded as not yet confirmed,[8] the simple hypothesis of Arrhenius and Walden will be followed in the present paper. It will be assumed that ionic mobility is not a function of ionic concentration.

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[1] For a review of the subject and a list of references see Wegscheider (*Z. physik. Chem.*, 69, 603 (1909)) and Partington (*J. Chem. Soc.*, 97, 1162 (1910)).

[2] Jahn, *Z. physik. Chem.*, 33, 545 (1900); 35, 8 (1900).

[3] Arrhenius, *Ibid.*, 36, 28 (1901).

[4] For references see Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

[5] Lewis, THIS JOURNAL, 34, 1631 (1912).

[6] Arrhenius, *Z. physik. Chem.*, 31, 197 (1899). See also Franklin and Kraus, THIS JOURNAL, 27, 216 (1905); Lewis and Wheeler, *Z. physik. Chem.*, 56, 179 (1906).

[7] Walden, THIS JOURNAL, 35, 1649 (1913).

[8] Wegscheider, *Z. physik. Chem.*, 69, 605 (1909).

When we consider higher concentrations, the mobilities of the ions undoubtedly vary. Also the different ions of an electrolyte are not equally affected by the change in the nature of the medium, since the transport numbers may vary appreciably with the concentration.[1] This variation is clearly connected with the phenomena of ionic hydration, and is important only in the case of electrolytes containing highly hydrated ions, where the variation in the degree of ionic hydration with the concentration will be greatest. For more normal electrolytes the change in the transport numbers of the ions, for solutions of less than normal concentration, may be regarded as of secondary importance.[2]

From the point of view taken above--that the ionic mobility is, in normal cases,[3] not a function of the ionic concentration--it follows that the degree of accuracy obtained in the determination of γ, as calculated from the experimental value for Λ, will be dependent primarily only upon the accuracy of the viscosity correction applied. This correction has already been discussed in an earlier section.

The fundamental assumption of Arrhenius, even if it does not lead us directly to conclusive results, yet enables us to attack problems which we should otherwise have to leave untouched. It has consequently been in general use in the investigation of concentrated solutions as our only means, until considerable advances have been made, of interpreting and using experimental results.[4]

The Change from Volume to Weight Units of Concentration.—From a purely thermodynamic and theoretical view point, there is no question as to the desirability of the change from volume to weight concentration units,[5] here as in other branches of physical chemistry. From the experimental side the use of the volume unit undoubtedly offers many advantages in simplicity and convenience of procedure, and these suffice to account for its general adoption for the expression of experimental data. However, since Λ has the same value expressed in either unit, the change of units here involves no experimental difficulties to counterbalance its advantage for the expression and derivation of theoretical relations.

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[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), page 201 In the case of two only of the simple uni-univalent electrolytes given is the variation in the transport number of the anion, between zero and half-normal concentration, greater than 0.01. These two electrolytes are the chlorides of lithium and sodium, the component ions of which are known to be highly hydrated.

[2] The accurate determination of transport numbers is extremely difficult, and in most cases a large variation in the transport number represents a relatively small change in the calculated value of γ.

[3] *i. e.*, where the variation in the degree of ionic hydration with concentration exercises no disturbing influence.

[4] Compare Lewis, *Z. physik. Chem.*, **70**, 217–8 (1910).

[5] Planck, *Wied. Ann.*, **32**, 489 (1887); Washburn, THIS JOURNAL, **32**, 668 (1910).

In several branches of physical chemistry, closely related to equivalent conductivity, the change to weight units has already furnished important results. A prominent example is afforded by the work of Morse and Frazer[1] on the osmotic pressures of solutions of sucrose. Results of experiments on the lowering of the freezing point, the raising of the boiling point, and the lowering of the vapor pressure of the solvent by dissolved salts have always been expressed in weight units of concentration.[2] In the application of the solubility-product principle, the concentrations of the dissolved electrolyes must be reduced to weight units to obtain comparable results.[3] Similarly, the viscosity of binary mixtures[4] (including solutions) has been shown to be a function of the molecular and not of the volume concentration of the two components. This is important in view of the close relation existing between viscosity and equivalent conductivity.

Experimental Data.—In the preceding section the modified form of the dilution law has been shown to be fundamentally more simple than the original dilution law, and to cover a more extended range, since it is exactly applicable to concentrated solutions. Hence it is, at this point, legitimate to emphasize the theoretical basis assumed above, namely, that the dissociation of the undissociated molecule in the solution is brought about, not spontaneously, but by the action of the solvent.

It is not asserted here that the above theoretical basis is definitely established by the results obtained. Several factors have been left out of consideration, which become of importance in concentrated solutions, as is discussed later; also the amount of *exact* experimental data that can be brought forward is, at present, extremely meagre.[5]

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[1] Morse and Frazer, *Am. Chem. J.*, 34, 1 (1905); see also Bancroft, *J. Phys. Chem.*, 10, 319 (1906), and Morse, Frazer and Dunbar, *Am. Chem. J.*, 38, 212–26 (1907).

[2] For example, in the freezing point data, collected by Noyes, THIS JOURNAL, 32, 1026 (1910). In comparing the results obtained with those derived from conductivity experiments, however, Noyes has transferred these figures to volume concentrations without correction (THIS JOURNAL, 34, 485 (1912)). Washburn and MacInnes, in a similar comparison of the freezing point and conductivity data for solutions of caesium nitrate, have, on the other hand, expressed all quantities in molecular concentrations, THIS JOURNAL, 33, 1711 (1911).

[3] Kendall, *Proc. Roy. Soc.*, (*A*) 85, 200 (1911).

[4] Kendall, *Meddel. från K. Vet. Akads. Nobelinstitut*, Band 2, No. 25 (1912).

[5] Only very weak acids and bases are of use for examination here, since even in acids a little stronger than acetic acid we shall have, in *concentrated* solutions, the "anomaly of strong electrolytes" beginning to appear. The substances examined must also be very soluble in water to give sufficiently concentrated solutions. These conditions cut out the majority of the ordinary organic acids, and only in a few of those remaining are all the necessary data available.

An extensive list of weak electrolytes has been tabulated by Wegscheider,[1] and the concentration fixed in each case at which divergence from the dilution law begin to become appreciable. For all these electrolytes, it may be asserted that the modified dilution law will give *qualitatively* better agreement with the experimental data at high concentrations, but the absence of reliable density and viscosity results precludes, at present, the possibility of establishing *quantitatively* exact agreement.

Experiments are already in progress to supplement the few instances given below.

For the series of normal fatty acids, the following results are available. The conductivity data are selected from the determination of White and Jones;[2] the results for viscosity and density are taken from the work of Reyher.[3] The various columns have the same significance as in Table I.

TABLE III—FATTY ACIDS, 25° (WHITE AND JONES).

Acid	v	Λ.	η.	d	100 K.	100 K_2.
Acetic.	2	2.089	1.060	1.0042	0.00169	0.00194
	8	4.342	1.017	1.0013	0.00183	0.00191
	32	8.699	1.004	1.0003	0.00186	0.00188
Propionic.	2	1.700	1.099	1.0035	0.00116	0.00145
	8	3.704	1.026	1.0011	0.00138	0.00147
	32	7.436	1.007	1.0003	0.00141	0.00143
n-Butyric.	2	1.730	1.132	1.0022	0.00120	0.00161
	8	3.891	1.031	1.0006	0.00153	0.00164
	32	7.902	1.008	1.0002	0.00159	0.00162
iso-Butyric	2	1.633	1.129	1.0016	0.00108	0.00152
	8	3.821	1.032	1.0004	0.00147	0.00158
	32	7.621	1.008	1.0001	0.00148	0.00150

Considering the accuracy of the data employed, the degree of concordance in the values shown under 100 K_2 in the above table is satisfactory throughout. Hence the modified dilution law may be held to apply, for the above acids, up to solutions of at least half-normal concentration.

In Table IV the figures for a typical weak base —ammonia— are given.

TABLE IV.—AMMONIA, 25° (OSTWALD).

v.	Λ.	η.	d	100 K	100 K_2.
2	1.56	1.012	0.995	0.00193	0.00203
4	2.24	1.006	0.997	0.00199	0.00204
8	3.21	1.003	0.998	0.00205	0.00208
16	4.55	1.001	0.999	0.00207	0.00208
∞	(252)	.	. .		. . .

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[1] Wegscheider, *Z. physik. Chem.*, **69**, 611–13 (1909).

[2] White and Jones, *Am. Chem. J.*, **44**, 159 (1910).

[3] Reyher, *Z. physik. Chem.*, **2**, 749 (1888). The viscosity results are liable to (relatively) considerable error, as will be evident by inspection of the original.

The conductivity results are those of Ostwald,[1] the viscosity and density data are interpolated from the figures given in Landolt-Börnstein.

The agreement of the values given under 100 K_2 is again satisfactory, in view of the nature of the experimental data. For example, an error of 0.01 in the value of Λ, at the first concentration given, corresponds to a difference of 3 units in 100 K_2.

The above tables may be amplified by extending the modified form of the dilution law to the author's equation for transition electrolytes, shown in equation (3), (which also fails in concentrated solutions) and testing its applicability there also. Equation (3) is modified to the form:

$$\gamma^2/(1-\gamma)v' = K + c\,(1-\gamma)/\gamma. \qquad (9)$$

The results for a typical transition electrolyte—dichloroacetic acid— are given in Table V. The viscosity and density figures are taken from the determinations of Kanitz.[2]

TABLE V —DICHLOROACETIC ACID, 25° (KENDALL)

				$100\{K+c(1-\gamma)/\gamma\}$		$100\{K+c_2(1-\gamma)/\gamma\}$	
v	Λ	η.	d	Expt	Calc	Expt	Calc
2	114.9	1.1318	1.0263	6.33	7.68	8.92	8.93
4	151.7	1.0640	1.0139	6.38	6.70	7.57	7.52
8	190.2	1.0287	1.0067	6.00	6.08	6.60	6.62
16	231.6	1.0143	1.0033	5.64	5.65	5.96	6.00
32	273.1	1.0071	1.0016	5.38	5.34	5.57	5.55
64	309.7	1.0035	1.0008	5.12	5.14	5.23	5.26
128	338.7	1.0018	1.0004	4.96	5.02	5.04	5.09
256	359.2	1.0009	1.0002	4.94	4.94	5.02	4.99
∞	385.6	....			4.85	.	4.85

$K = 0.0485$, $c = 0.0120$, $c_2 = 0.0173$

The agreement of equation (3) in its original form with the experimental results is shown by the figures under $100\{K + c.(1-\gamma)/\gamma\}$ in Table V, the agreement of the equation in its modified form (9) is given by the figures under $100\{K + c_2(1-\gamma)/\gamma\}$. It will be seen that the equation holds exactly, in its original form, only for dilute solutions; while the modified form gives agreement throughout the entire series.

Additional experimental results will be given in a future communication, where the application of the above changes to solutions of strong electrolytes will also be considered. In conclusion here, the limits of the applicability of the modified dilution law proposed are briefly examined, and the results obtained in this paper compared with those of Walden.

Limits of Applicability of the Modified Dilution Law.—It has been shown that the dilution law, in its modified form, is exactly applicable up to concentrations of at least half-normal for typical weak electrolytes. In the case of acetic acid, the values obtained for K with the aid of the modified law are constant up to concentrations well above normal, then follows a decrease when still higher concentrations are considered.

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[1] As transposed to the modern units in Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), page 167.

[2] Kanitz, *Z. physik. Chem.*, **22**, 336 (1897).

It will be evident, on examination, that the modified law *must* break down at these very high concentrations of solute, since many complicating factors arise which have not been taken into account. The chief of these are enumerated below.

In the first place, the viscosity correction to Λ becomes larger, and the probable error of its application greater, with increase of concentration. Also the likelihood that the fundamental assumption of Arrhenius, discussed previously, will be true even if an exact viscosity correction could be applied, decreases as the concentration of solute is increased.

At high concentrations, further, the hydration of the solute—both in its undissociated and in its dissociated state—complicates the equilibrium in the solution. The undissociated solute, if hydrated, will withdraw a considerable quantity of solvent from the equilibrium, and the concentration of "free" solvent in the solution will be greatly reduced. If the ions are hydrated, their mobilities may vary considerably in concentrated solutions, owing to the variations in the degree of hydration with the concentration of the solvent.

More important still, the change in the *nature* of the solvent at high concentrations of solute will be considerable. A highly associated solvent, such as water, will tend to dissociate more and more into simpler molecules as its concentration in the solution decreases.[1] Also the change in the dielectric constant of the medium, for high concentrations of solute, is of importance.

Finally the variation in the heat of dilution with the concentration (which affects the constancy of K) has not been taken into consideration.

The modified form of the dilution law, as expressed in the simple equations (7) and (F′), cannot be expected to hold in general, therefore, for *highly concentrated* solutions. Only up to (approximately) normal concentration of solute is it exactly valid. Even so, this represents a considerable advance upon the previous limit of $v = 32$ (approximately) for the dilution law in its original form.

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[1] The ionizing power of a solvent is intimately connected with its *power of association* into large molecules. The best ionizing solvents are unsaturated, *e. g.*, water contains an unsaturated oxygen atom with two free valencies, and the simple molecule may be written $H_2O\underset{-}{+}$. Hence, by the loss of two free valences (the positive charge on one oxygen atom being neutralized by the negative charge on another) two simple molecules can combine to form a complex molecule, $+OH_2\,H_2O-$. Such association can evidently continue further, each step being accompanied by the loss of two free valences. "One can readily see that such molecules would be electrically polarized, and their charges might easily have the power to cause electrolytic dissociation or ionization." Stieglitz, "Qualitative Chemical Analysis" (1912), Part 1, page 65. Compare also Arrhenius, "Theories of Chemistry" (1907), page 83.

Comparison with the Results of Walden.—It is of interest at this point to compare the conclusions of the present investigation with those drawn by Walden from the study of the dielectric constants of dissolved salts, and to examine how far the results may be combined.

The hypothesis advanced here as an explanation of the immediate cause of the dissociation of the undissociated molecule in the solution of an electrolyte is that the simple undissociated molecules are broken up into their component ions by impact with the molecules of the solvent.

Walden,[1] on the other hand, concludes that "the process of disaggregation of the polymerized salt molecules also causes, and induces, the process of ionic cleavage." The following processes are assumed.[2]

$$(\mathrm{MeX})_x \rightleftharpoons (\mathrm{MeX})_{x-1} + \mathrm{MeX} + \oplus\ominus. \quad \text{(I) Depolymerization.}$$

$$\mathrm{MeX} + \oplus\ominus \longrightarrow \mathrm{Me}\oplus + \mathrm{X}\ominus. \quad \text{(II) Ionization.}$$

$(\mathrm{MeX})_x$ is the polymerized salt, x the extent of association, MeX the simple salt molecule. $\oplus$ and $\ominus$ represent a positive and a negative electron, respectively, $\oplus\ominus$ a neutral electron (neutron),[3] Me $\oplus$ a cation, X $\ominus$ an anion.

Now the depolymerization of the solid salt $(\mathrm{MeX})_x$, which takes place in its solution, must be regarded as due to the bombardment of the complex and unstable molecules of the salt by the molecules of the solvent. The reaction is specific in each case, and the natures of both solute and solvent are factors in the degree of depolymerization. That this is so is shown by the two facts that different substances are depolymerized to different degrees in the same solvent, and that the same substance is depolymerized to different degrees in different solvents.

In this depolymerization of the solute, neutrons are formed in the solution, as is indicated by the first equation of Walden above. These neutrons will attach themselves to molecules of the solvent,[4] and the dielectric constant of the medium will be changed.

The process can be studied from another point of view with similar resalts. After the addition of the salt, the concentration of the solvent in the solution will have been diminished, hence its degree of association will also have diminished. That is, some complex molecules of the solvent will have broken down into simpler molecules, and this process is essentially *the taking-up of neutrons.*[1] For example, in water,

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[1] Walden, THIS JOURNAL, 35, 1661 (1913)

[2] The depolymerization process (Equation I) consists, of course, of successive stages from $(\mathrm{MeX})_x$ to MeX, of which one only is given above.

[3] Walden's conception of "neutral electrons" is retained in the discussion merely for convenience in the comparison of results. It will become evident below that the argument could be more logically expressed in terms of *free valences*, without the use of the indefinite expression "neutron."

[4] This statement is, of course, an assumption, since the neutrons might attach themselves directly to the simple undissociated molecule MeX. (Compare A. A. Noyes, *Carnegie Institute Publication*, No. 63, 351 (1907).) The change in the degree of association of the solvent with the concentration of solute necessitates, however, at least *some* transfer of neutrons to the solvent.

$$(H_2O)_n^+ \rightleftharpoons (H_2O)_{n-1}^+ + (H_2O)^\pm. \qquad (10)$$

We may therefore rewrite the first equation of Walden in the form:

$$(MeX)_x + (H_2O)_n^+ \rightleftharpoons (MeX)_{x-1} + MeX + (H_2O)_{n-1}^\pm + (H_2O)^+.$$

It is evident from this equation that *the process of depolymerization is common to both solvent and solute,*[2] and is accompanied by an increase in the number of neutrons in the solution and by a change in the dielectric constant. The change in the dielectric constant will be greater, the more neutrons the solvent has taken up, that is, the greater the degree of depolymerization.[3] This is in accordance with the results of Walden, and is of importance in the consideration of the "anomaly of strong electrolytes."

It is now evident that the second equation of Walden, for the expression of the ionization equilibrium, can be at once made identical with the equation given on page 1078 of the present paper by transformation as below:

$$MeX + [H_2O]^+ \rightleftharpoons Me \oplus + X \ominus ,$$

the solvent acting *simply as the carrier of the "neutron."* Hence also the equation

$$c_u . c_s / c_i^2 = K' \qquad (7)$$

for the dissociation process can hold only so long as the concentration of neutrons in the solution is proportional to the concentration of the solvent. At high concentrations this can no longer be assumed to be the case, and the modified dilution law consequently cannot apply exactly, as has already been pointed out in the previous section.

We have now a simple means of expressing the mechanism of electrolytic dissociation. By impact of an undissociated molecule of the solute, MeX, with a molecule of the solvent, a neutron is transferred from the latter to the former, and the undissociated salt breaks up into its separate ions Me $\oplus$ and X $\ominus$. Similarly, by impact between ions of unlike charge, Me $\oplus$ and X $\ominus$, a molecule of the undissociated salt MeX is formed, with the liberation of a neutron, which attaches itself to a molecule of the solvent. The solvent molecules thus lose and gain neutrons alternately, as expressed by equation (10). The above view is evidently consistent with the fact that ionizing solvents possess the two characteristic properties of *unsaturation* (presence of neutrons) and *association*.

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[1] See note on page 1085. A neutron is equivalent to *two free valences*, and is used in this sense throughout the present discussion.

[2] Hence, also, non-associated solvents do not depolymerize dissolved salts. Consequently salts are highly ionized only by associated liquids; for example, hydrochloric acid, which is almost entirely dissociated in water, gives practically a non-conducting solution in benzene (Kablukoff, *Z. physik. Chem.*, 4, 430 (1889)).

[3] It is possible that the dielectric constant is *directly* a function of the concentration of neutrons on the solution. This will account for the low dielectric constants of non-associated liquids, and for the great increase in the dielectric constant of a feebly ionizing solvent on the addition of an electrolyte.

By comparison of the results of Walden with those of the present paper and by combination of the conclusions drawn we are able to obtain, therefore, a simple view of the whole mechanism of the dissociation equilibrium in the solution of an electrolyte.

Summary.

A modified form of the dilution law has been proposed, which is found to be in accordance with the data of experiment throughout a region in which the dilution law, in its original form, fails to apply, namely in concentrated solutions of weak electrolytes.

The theoretical basis underlying this modification of the dilution law is that the dissociation of the undissociated molecule RX in the solution of a binary electrolyte, into its component ions R^+ and X^-, takes place not spontaneously but by impact with the molecules of the solvent.

With the use of this hypothesis the dilution law, as derived thermodynamically, is found to be fundamentally simpler in form than previously, since it is applicable exactly not only to dilute but also to concentrated solutions without any simplifying assumptions.

The advantage of a change from volume units of concentration to weight or molecular units, for the expression of equivalent conductivities and the calculation of dissociation constants, has been pointed out.

The conclusions of the present investigation have been compared and combined with those of Walden, with the result that a simple view of the mechanism of the ionization equilibrium is obtained. It is shown that the dissociating power of the solvent molecules is to be ascribed to their unsaturated character, *i. e.*, to the presence of free valences.

Additional experimental results will be given, and the case of strong electrolytes examined, in a future communication.

The above investigation was commenced at the Nobel Institute of Physical Chemistry, Experimentalfältet, Sweden. It is a pleasant duty to me to express here my gratitude to Professor Svante Arrhenius for his hospitality, and for his helpful criticism of the initial stages of the research.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD COLLEGE.]

THE RESISTANCE OF PLATINUM VESSELS TO HOT NITRIC ACID.

BY GREGORY PAUL BAXTER AND FRED LESLIE GROVER

Received March 31, 1914

In a recent research upon the atomic weight of selenium, Jannek and Meyer[1] have investigated the corrosion of platinum by hot nitric acid, and have made the astonishing statement that 10 cc. of halogen-free nitric acid distilled through a platinum condenser, upon evaporation in a platinum crucible yielded 0.00228 g. of non-volatile material. Since these investigators call attention to the fact that in a research by one of us[2] nitric acid was purified by distillation through a platinum condenser, and imply that the acid thus prepared was not pure, and since nitric acid has been thus purified in the Harvard Chemical Laboratories for many years, we have decided to renew the study of this subject, although the matter has several times before been considered, and this method of purification has been found to be adequate.

Evidence has already been published on the subject by Richards,[3] who states that nitric acid distilled through properly cleaned platinum leaves no weighable residue upon evaporation. Moreover, Richards and Willard[4] in an investigation upon the atomic weights of silver, lithium and chlorine, have found that a platinum dish when digested for some time with concentrated nitric acid did not lose appreciably in weight.

Our experiments upon this subject are described below: About 800 cc. of commercial C. P. acid were placed in a one-liter Jena glass flask with a constricted neck fitted to a quartz condenser. The condenser generally used for such purposes in this laboratory[5] consists of a 1 cm. tube, either of quartz or platinum, with a right angle bend about 5 cm. from one end. The short arm is inserted into the constricted neck of a Jena glass flask, making a joint which eventually becomes sealed with condensed liquid, and allowing a refluxing of the boiling liquid. Furthermore, liquid which condenses on the glass flows back into the flask instead of into the condenser. The long arm of the tube, about 30 cm., is water-jacketed to serve as a condenser. Two-thirds of the nitric acid was distilled off and rejected, since, as has been repeatedly shown in this laboratory, such treatment is necessary to remove the last traces of hydrochloric acid, even when the original acid is comparatively pure.[1] Next, the condenser was steamed out with nitric acid vapor for five minutes, and then 20 cc. of the distillate were collected in a weighed quartz crucible. After slow evaporation over an electric stove, no visible or weighable residue remained. During the evaporation the crucible touched nothing but a clean platinum triangle, and was carefully covered. A second experiment gave the same result. These observations are in perfect accord with similar experiments of Jannek and Meyer.

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[1] *Z. anorg. Chem.*, **83**, 51 (1913).

[2] Baxter and Moore, THIS JOURNAL, **34**, 1644 (1912); *Z. anorg. Chem.*, **80**, 185 (1913).

[3] *Proc. Am. Acad.*, **26**, 248 (1891).

[4] *Publ. Carnegie Inst.*, No. **125**, 17; THIS JOURNAL, **32**, 18 (1910); *Z. anorg Chem.*, **66**, 247.

[5] Richards, *Proc. Amer. Acad.*, **30**, 380 (1894); Richards and Willard, *Publ. Carnegie Inst.*, No. **125**, 15 (1910); THIS JOURNAL, **32**, 16; *Z. anorg. Chem.*, **66**, 245.

The purest nitric acid was now distilled in the same manner as before, but through a platinum condenser, well seasoned by more than twelve years' continual use, and was caught in a large, acid-seasoned quartz flask. After 300 cc. of this acid had been evaporated in a weighed quartz crucible, with all the precautions described above, only 0.00003 g. of whitish material remained. This experiment, in contradiction to the evidence of Jannek and Meyer, shows conclusively that practically nothing is extracted from pure, well-cleaned platinum by hot concentrated nitric acid.

Further experiments were carried out with an old platinum still of the goose-neck type, fitted with a second platinum condenser. The distillate was collected this time, however, in a well-seasoned platinum dish of 100 cc. capacity and about 40 g. weight, which had previously been twice cleaned by fusion with potassium pyrosulfate and subsequent boiling with nitric acid. After 200 cc. of distillate had been evaporated to dryness in this dish, a very slight brownish residue remained, and the dish weighed 0.00003 g. more than at first. It is evident that no important amount of material was extracted from the condenser. Gentle ignition for a moment caused the dish and contents to lose in weight by 0.00007 g., *i. e.*, the weight was now 0.00004 g. less than the original. The residue was now removed by warming with hydrochloric acid, and the dish was washed, dried and gently ignited. This treatment caused a further loss in weight of 0.00007 g., so that the total loss in weight of the dish was 0.00011 g. Undoubtedly a portion of this loss was caused by solution of the platinum in hydrochloric acid in the presence of air. These changes in weight are, however, scarcely greater than the probable error of weighing a dish of so large a weight and surface as this one. One can hardly believe that the nitric acid had an appreciable effect on either still or dish.

The slight, dark-colored residue obtained in the above experiment led us to suspect that the dish itself might have been attacked by the nitric acid. Therefore, 100 cc. of nitric acid, which had been distilled through a quartz condenser, was evaporated in it. Such acid has been shown above to be free from dissolved impurities. A residue identical in appearance with the previous one was obtained, and the dish gained in weight by 0.00003 g. When this residue was rubbed off with a clean finger, and the dish carefully washed and ignited, the weight of the dish was found to be 0.00006 g. more than at first. As suggested before, fluctuations in weight of the magnitude of these are not significant. The fact that a similarly appearing residue was obtained by evaporation of both specimens of nitric acid, indicates, however, that the real source of the very slight residues was the dish and not the condenser.

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[1] Jannek and Meyer do not state how hydrochloric acid was removed from their nitric acid

The dish used in these experiments had been used for some time for various purposes, so that the more soluble surface impurities had undoubtedly been removed even before the cleaning with potassium pyrosulfate, to which we subjected it preliminary to our experiments. However, with platinum vessels which have not been subjected to drastic cleaning processes, there is no question that the danger of solution of surface impurities is not only real but serious. For instance, in one experiment 30 cc. of nitric acid which had been distilled through a platinum condenser was evaporated in a *new* platinum crucible, which had been merely washed and ignited. In this experiment the crucible gaintd 0.00030 g. And even after the crucible had been twice cleaned wieh potassium pyrosulfate, and boiled with nitric acid, in three repetitions of the experiment in which a quartz condenser was used, gains of 0.00018, 0.00002, and 0.00002 g. were observed.

In two cases the residues obtained in platinum were tested for iron with thiocyanate. Although traces of iron were found, the amounts were far too small to explain even the slight residues observed.

It is worth calling attention to the fact that the danger from surface impurities in the platinum has always been recognized in the Harvard Laboratories, and that new platinum vessels are always thoroughly cleaned before use, either by fusion with pyrosulfate or by sublimation of ammonium chloride from the vessel, according to Stas's suggestion, or by both methods.

The first fact established by these experiments is that, in harmony with the observations of Jannek and Meyer, concentrated nitric acid distilled through quartz contains no perceptible quantity of dissolved impurities; and the second that nitric acid distilled through well-seasoned platinum is of equal purity. The very small residues observed in the foregoing experiments came, no doubt, from the platinum vessels in which the evaporations took place, owing to the superficial oxidation of the baser metals. The surprisingly large residues reported by Jannek and Meyer are probably to be attributed either to the use of vessels of impure platinum, to inefficient cleaning of the platinum vessels, or to the presence of traces of hydrochloric acid in the nitric acid employed.

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DETECTION OF CYANIDES IN THE PRESENCE OF FERRO- AND FERRICYANIDES AND THIOCYANATES.

By O. L. Barnebey.

Received March 25, 1914

The reaction upon which this detection is based is the solubility of copper sulfide in solutions of alkali cyanides. When hydrogen sulfide is passed into a dilute ammoniacal cupric solution a precipitate of cupric sulfide is formed, or a deep blue to brownish black coloration is imparted to the solution, depending upon the amount of hydrogen sulfide dissolved, the temperature, and the dilution of the solution. The addition of an alkaline cyanide clears this suspension or colored solution. The copper solution can be made so dilute that the test becomes quite delicate, much more delicate than the bleaching of the blue solution of copper ammonia compounds, and has the additional merit of not being interfered with seriously by ferro- or ferricyanides, or thiocyanates.

An ammoniacal copper solution was prepared by dissolving 1.25 g. $CuSO_4.5H_2O$ in water, making ammoniacal and diluting to a liter. Each cubic centimeter of this solution is equivalent to about 0 000473 g. of hydrocyanic acid on the basis of the following reaction, which, however, is empirical:

$$2[CuSO_4.4NH_3] + 7KCN + 7H_2O = 2K_2Cu(CN)_3 + KCNO + K_2SO_4 + (NH_4)_2SO_4 + 6NH_4OH$$

The test is performed as follows: A bubble or two of hydrogen sulfide gas is passed into, or a few drops of hydrogen sulfide water are added to a small quantity of the standard copper solution, the amount of this depending upon the delicacy desired. This suspension is then added to the unknown ammoniacal solution (or *vice versa*) with constant shaking. If the color is bleached, the presence of a cyanide is indicated. The addition of the ammoniacal copper solution is continued until no further bleaching is noticed. From the volume of copper solution used an approximate quantitative estimation can be made. With care, one can add a few cubic centimeters of dilute hydrogen sulfide water in the cyanide titration of copper at the instant of bleaching and obtain a coloration which is then bleached with more cyanide, making a moderately accurate end point. In the presence of ferrocyanides, however, the reaction is not quantitative, inasmuch as the ferrocyanide is oxidized to ferricyanide more or less completely during titration.

The color caused by 0.1 cc. of the copper solution in a volume of 5 cc. is bleached by 0.2 cc. of a 0.01 *N* solution of KCN when the test is made as above indicated, which means a delicacy of about 1.0 parts HCN per hundred thousand.

In the presence of 50 cc. of a solution of KCNS (equivalent to 2 g.) 0.5 mg. of HCN can be detected; 50 cc. of a 4% solution of $K_4Fe(CN)_6$

(2 g.) allows a detection of 1 mg. of HCN; while 50 cc. of a 4% solution of $K_4Fe(CN)_6$, (*i. e.*, 2 g.) will likewise permit a detection of 0.5 mg. of HCN. In the presence of small quantities of the above cyanogen compounds the test is reliable to 0.1 mg. of HCN.

In the presence of smaller amounts of ferro- or ferricyanides the test becomes correspondingly more delicate. When the test is applied to solutions containing much ferricyanide, one should add as much copper solution to a blank, containing approximately the same amount of ferricyanide, as to the solution being tested for cyanide and the difference in shade should be noted, or the quantities of copper solution necessary to give a certain depth of color should be compared.

For the average requirements of qualitative analysis, tenth-normal copper sulfate solution will suffice.

Inasmuch as the test gives a decided reaction for relatively small amounts of cyanides, and also furnishes an indication of the relative amount present in the solution examined, as well as being applicable in presence of other cyanides, this test is proposed for general qualitative purposes.

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[CONTRIBUTION FROM THE ANALYTICAL LABORATORY, COLLEGE OF THE CITY OF NEW YORK.]

A NEW PROCEDURE FOR THE SEPARATION OF THE COPPER AND TIN GROUPS.

BY LOUIS J. CURTMAN AND JOSEPH K. MARCUS

Received February 20, 1914

Despite the many shortcomings of the ammonium polysulfide method for the separation of the copper and tin groups, no procedure has ever been devised whereby a sharp separation of these groups from each other might be obtained. The objections to the ammonium polysulfide method, as shown by the work of A. A. Noyes,[1] are as follows:

1. Ammonium polysulfide dissolves some copper sulfide[2] and mercuric sulfide,[3] thus making the separation of these metals incomplete, and at the same time causing confusion by their precipitating with the metals of the tin group.

2. Under certain conditions a large quantity of tin[4] remains undissolved by the ammonium polysulfide.

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[1] THIS JOURNAL, 29, 170.

[2] 5 to 10 mg. of copper may dissolve in the ammonium polysulfide when a large amount of copper is present.

[3] 0.5 to 1 mg. of mercury may dissolve in ammonium polysulfide when a large amount of mercury is present.

[4] When large quantities of elements of the copper group and only 3 to 5 mg. of tin are present, the whole of the tin may remain undissolved and when much cadmium is present, together with tin in the stannous state, as much as 15 mg. of the latter may be left in the residue.

3. When the ammonium polysulfide filtrate is acidified with hydrochloric acid, a heavy precipitate of sulfur usually comes down, thus obscuring the presence of sulfides of the tin group.

There are three other reagents which are in use, or have been suggested for use to effect the separation of the divisions of the hydrogen sulfide group. They are sodium carbonate, sodium hydroxide, and potassium hydroxide.

The Sodium Carbonate Method.—This method, we are informed, was devised by H. T. Beans and is in use at the present time at Columbia University. A brief outline of this method is also given by Hinds.[1] The method as given in the unpublished notes of H. T. Beans may be briefly summarized as follows:

The precipitated sulfides of the hydrogen sulfide group are treated with a mixture of 25 cc. of 3 N sodium carbonate and 20 cc. of 3% hydrogen peroxide solutions. The mixture is then diluted to 200 or 300 cc. and warmed gently (not over 50°). A few bubbles of hydrogen sulfide are now passed into the solution, and, if a black precipitate appears, more hydrogen sulfide is passed in until precipitation is complete. The residue now contains the metals of the copper group, and the filtrate, those of the tin group.

The notes from which the authors got the method showed that it had not been sufficiently worked out to determine its efficiency. It was therefore thought worth while to investigate the possibilities of this method as a substitute for the ammonium polysulfide separation.

A great number of experiments and test analyses were carried out according to the procedure as given in the notes referred to above. Lack of space does not permit us to give the results of these experiments in full, but suffice it to say that the sodium carbonate and hydrogen peroxide method was found to be thoroughly inadequate in effecting the separation of the two groups from each other, because whenever antimony was present, it was found that, on adding the sodium carbonate and hydrogen peroxide to the precipitated antimony sulfide, about one-half of the antimony came down from the solution in the form of a heavy white flocculent precipitate.[2] The complication which such a state of affairs would cause in an analysis is quite evident. Not only would the test for antimony in the tin group be rendered considerably less delicate, but in

[1] "Qualitative Analysis," page 91

[2] To determine the amount of antimony which remained undissolved by the sodium carbonate and hydrogen peroxide treatment, separate solutions containing 50 mg. and 250 mg., respectively, of antimony as antimony trichloride were completely precipitated as sulfide, and treated with a mixture of sodium carbonate and hydrogen peroxide, in accordance with the directions given in the notes of Beans. The white residues, which remained unacted upon by this treatment, after having been washed to acid reaction with hot water slightly acid with hydrochloric acid, were then dissolved in strong

addition, the antimony remaining undissolved would give rise to complications in the analysis of the copper group. There are, moreover, some minor objections to this method, but it was not thought worth while to go into them, inasmuch as the incomplete separation of the antimony was sufficient to condemn the method.

The Separation by Means of the Caustic Alkalies.--The action of the caustic alkalies in dissolving the sulfides of the tin group and leaving the sulfides of the copper group unacted upon is mentioned in nearly all the texts on qualitative analysis. However, a search of the literature revealed only one instance where any attempt was made to work up a scheme of separation by means of the hydroxides of sodium and potassium.[1] A brief outline of the method of J Walker[2] is as follows:

The precipitated sulfides of the hydrogen sulfide group are treated with caustic soda, a few drops of ammonium polysulfide being added to oxidize any stannous tin that may be present. Sodium peroxide is also added to the boiling sodium hydroxide solution in order to reprecipitate any mercuric sulfide present.[3] By this method the sulfides of arsenic antimony and tin are taken into solution, while the sulfides of the remaining metals are left in the residue.

The method is, however, open to objection for the reason that when antimony sulfide is treated with a mixture of sodium hydroxide[4] and sodium peroxide, a large proportion of the antimony always remains undissolved as a white precipitate.

It is thus apparent that none of the methods mentioned have anything to recommend them for use in the separation of the divisions of Group 2 in place of the ammonium polysulfide separation.

After much experimentation, the authors have devised a procedure for the separation of the copper and tin groups, which is free from the objections to the ammonium polysulfide separation, as mentioned above. Further, the method possesses the merit of adequately providing for the systematic detection of pentavalent arsenic.

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hydrochloric acid and analyzed for antimony by Weller's volumetric method. The solution containing 50 mg. showed approximately 30 mg. of antimony in the residue from the sodium carbonate treatment. The solution containing 250 mg., showed 125 mg antimony in the residue.

[1] In Clowe's "Qualitative Analysis," the caustic alkalies are suggested as a reagent for the separation of the divisions of the hydrogen sulfide group, but no provision is made for the complications which the use of this reagent involves. The use of the caustic alkalies is also suggested in F. M. Perkin's "Qualitative Analysis."

[2] J. Walker, *J. Chem. Soc.*, 83 (1903).

[3] According to Walker the solution of HgS is due to K_2S formed by the action of an excess of NaOH on a tin group sulfide. But no experimental evidence is offered (See Test Experiment 6.)

[4] When potassium hydroxide is used in place of sodium hydroxide, the antimony sulfide dissolves completely.

Procedure for the Analysis of the Filtrate from the Silver Group.

1. Precipitation of the Alkaline Earth metals and Part of the Lead.—Neutralize the filtrate[1] from Group 1 with NH_4OH and reacidify with 5 cc. HCl (1.19); add 8 cc. 20% H_2SO_4 and boil; cool and treat with an equal volume 95% alcohol. The precipitate is allowed to settle and the clear liquid decanted off through an ashless filter. Wash the precipitate once by decantation, keeping as much of it as possible in the beaker. The residue may consist of the sulfates of Ba, Sr, Ca and Pb. It is analyzed for these metals in accordance with the method given by Curtman and Frankel.[2]

NOTES.—1. The H_2SO_4 precipitates all the Ba and Sr and most of the Ca and Pb—about 10 mg. Ca and 15 mg. Pb pass into the filtrate. The Pb is subsequently detected in the H_2S precipitation, and the Ca by treating the filtrate from Group 3 with $(NH_4)_2C_2O_4$.

2. Precipitation of Group 2.—Boil down the filtrate from the H_2SO_4 treatment with constant stirring to one-half its volume.[2] Add 3 to 4 cc. HCl (1.19) and 75 cc. saturated SO_2 solution. Heat for 20 to 25 minutes. Boil down to one-half its volume, cool, render slightly alkaline with concentrated NH_4OH and just acidify with dilute HCl. Add exactly 2.5 cc. HCl (1.19) heat the solution to boiling and pass in H_2S for a few minutes. Without filtering dilute the solution to 120 cc. with cold water and treat again with H_2S till precipitation is complete. Filter. The filtrate is set aside for the analysis of Groups 3 and 5. The residue may contain the sulfides of Hg, Pb, Bi, Cu, Cd, As, Sb and Sn.

NOTES.—1. 3 to 4 cc. concentrated HCl are added to the filtrate from the H_2SO_4 and alcohol treatment in order to prevent the Sb from precipitating on dilution with SO_2 solution next added.

2. The function of the H_2SO_3 is two-fold· (*a*) To reduce pentavalent As to the more easily precipitated form; (*b*) to oxidize stannous salts to the stannic condition, in which higher valence the sulfide is soluble in KOH. The reactions which take place, according to Prescott and Johnson[3] are represented by the following equations:

$$(a)\quad 3SnCl_2 + SO_2 + 6HCl = 3SnCl_4 + H_2S + 2H_2O.$$
$$(b)\quad 6SnCl_2 + 2SO_2 + 6H_2O = Sn_6O_{10}S_2 + 12HCl.$$
$$(c)\quad 6SnCl_2 + 2SO_2 + 8HCl = SnS_2 + 5SnCl_4 + 4H_2O.$$

3. The solution after treatment with SO_2 is boiled down to one-half its volume to drive off the excess of SO_2, which, if present, would yield a precipitate of sulfur with H_2S.

4. When $SnCl_2$ is oxidized to $SnCl_4$ by SO_2, more or less H_2S is formed as shown in the equations above. Thus a little SnS_2 is frequently precipitated in the solution. Likewise, if any As or Sb is present, a little of the sulfides of these metals may form. With the exception of the As_2S_3, these precipitates are dissolved when the solution is concentrated to expel the excess of SO_2.

3. Separation of the Copper and Tin Groups.—Wash the precipitated sulfides three times with a saturated solution of NaCl containing H_2S. Transfer the precipitate to a beaker and boil for one and one-half minutes with 25 cc. 25% KOH solution.[1] Dilute with 35 cc. of cold water and pass in a few bubbles of H_2S.[2] Filter through a double filter. The residue, after washing with hot water is analyzed for Hg, Pb, Bi, Cu and Cd. To the clear filtrate, add 30 cc. 3% H_2O_2 and boil gently for one minute with constant stirring. If a black precipitate appears, filter on a separate filter and test for Hg by dissolving the precipitate in aqua regia and adding $SnCl_2$.

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[1] The volume should not exceed 30 cc.

[2] THIS JOURNAL, 34, 1493.

[3] "Qualitative Analysis," 5th edition, p. 86.

NOTES.—1. In washing the precipitated sulfides, NaCl is preferred to an ammonium salt, because the latter would tend to precipitate some Sn from the KOH solution of the potassium stannate formed on the addition of H_2O_2.

2. KOH dissolves the sulfides of As, Sb and Sn(ic), leaving the sulfides of Hg, Bi, Cu and Cd completely undissolved. PbS is dissolved to a slight extent, but is reprecipitated by a few bubbles of H_2S. More than a few bubbles of H_2S should be avoided, for reasons stated below in Note 4

3. Some of the sulfides have a tendency to pass through the filter, notably CdS. By passing the mixture through a double filter, a clear filtrate is obtained.

4. When a Sn group sulfide is dissolved in KOH, K_2S is always formed due to the action of the excess of KOH on the thio salt (see Test Exp. 6). The reactions may be looked upon as taking place in the following manner:

$$a. \begin{cases} As_2S_2 + 6KOH = K_3AsO_3 + K_3AsS_3 + 3H_2O. \\ Sb_2S_3 + 2KOH = KSbS_2 + KSbSO + H_2O. \\ 2SnS_2 + 4KOH = K_2SnO_2S + K_2SnS_3 + 2H_2O. \end{cases}$$

$$b. \begin{cases} K_3AsS_3 + 2KOH = K_2S + K_3AsS_2O + H_2O. \\ KSbS_2 + 2KOH = K_2S + KSbSO + H_2O. \\ K_2SnS_3 + 2KOH = K_2S + K_2SnS_2O + H_2O. \end{cases}$$

Some K_2S is also formed in consequence of the treatment of the KOH solution with H_2S.

5. If any HgS is present, it will be partly dissolved by the K_2S formed, as shown above, and consequently will appear in the filtrate along with the Sn group metals. The addition of H_2O_2 to the alkaline filtrate oxidizes the K_2S to the sulfate, thus causing the HgS to reprecipitate.[3]

4. *Treatment of the Filtrate for the Tin Group Metals.*—Boil down the filtrate from the H_2O_2 treatment to 50 cc. with stirring. While hot, quickly neutralize with concentrated HCl and add 10 cc. in excess. Heat the solution to boiling till clear. Add 50 cc. of a saturated SO_2 solution and heat for 20 to 25 minutes. Boil down to about 70 cc. Make slightly alkaline with concentrated NH_4OH and then just acid with dilute HCl. Add exactly 2.5 cc. HCl (1.19), heat to boiling and pass in H_2S for a few minutes. Dilute the mixture to 120 cc. with cold water and again saturate

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[1] 100 cc. of the KOH solution contains 25 g. of solid KOH.

[2] See Test Experiment 6.

[3] Walker, *J. Chem. Soc.*, 83 (1903), makes use of Na_2O_2 to reprecipitate the dissolved HgS. The authors use H_2O_2 first, to avoid the introduction of sodium which has a tendency to precipitate antimony; second because Na_2O_2 increases the concentration of the alkali.

with H_2S until precipitation is complete. The precipitate consisting of the sulfides of As, Sb and Sn, is treated in the usual manner.

NOTES.—1. The action of H_2O_2 on the As, Sb and Sn sulfides in KOH solution is to oxidize the arsenic sulfide to arsenic acid and the Sb and Sn sulfides to the higher oxides. Therefore, when the alkaline solution is acidified with HCl, the Sb and the Sn, for the most part, come down in the form of white amorphous precipitates. The longer these precipitates are allowed to stand, the more insoluble they become. The hot alkaline solution is therefore quickly neutralized with strong HCl and the precipitate formed immediately dissolved by an excess of this reagent.

2. The filtrate from the H_2O_2 treatment is boiled to destroy the excess of H_2O_2, which, if present, would oxidize the SO_2 next added.

3. The H_2SO_3 is added in order to reduce the arsenic acid to the arsenious condition, whereby precipitation with H_2S is more easily and completely accomplished.

4. In order to insure complete precipitation of the As, Sb and Sn, the aciditv of the solution must be carefully adjusted before the treatment with H_2S.

Test Experiments.

I.

The Action of Sodium Hydroxide[1] *on the Sulfides of Group 2.*—In order to determine whether NaOH could be used to separate the sulfides of the divisions of Group 2, the following experiments were carried out:

Separate solutions, each containing 500 mg. of one of the metals of Group 2, were completely precipitated with hydrogen sulfide, filtered, washed and boiled with stirring for 2 minutes with 25 cc. of a 20% NaOH solution.[2]

The sulfides of Hg, Cu, Bi and Cd were found to be completely insoluble.[3] PbS dissolved to a small extent (about 1 mg.), but was completely reprecipitated on passing a few bubbles of H_2S into the alkaline solution. As_2S_3, As_2S_5, Sb_2S_3, and SnS_2 were practically completely soluble[4] in the caustic soda. SnS, at times, dissolved almost completely, leaving behind only a very small black residue, which was most likely some form of metallic tin, as shown by the solvent action of HCl upon it with the evolution of hydrogen. At other times, nearly all of the SnS remained undissolved by the sodium hydroxide.

Of interest are a few experiments which were performed with mixtures of SnS with As_2S_3 and Sb_2S_3, respectively:

1. A mixture of 300 mg. As, as a HCl solution of As_2O_3, and 200 mg. Sn, as $SnCl_2$, was completely precipitated with H_2S, filtered, washed, and treated with 25 cc. of a 20% NaOH solution. After boiling the mixture from 2 to 5 minutes, a heavy brownish black precipitate remained undissolved. The filtrate from this precipitate gave good tests for both As and Sn. The residue, after washing with hot water slightly acidified with HCl, was boiled with strong HCl, diluted and filtered; the filtrate gave a good test for Sn. The residue which remained from this treatment was treated with concentrated HNO_3 in which it readily dissolved with the evolution of oxides of nitrogen. The resulting solution, after reduction with SO_2, was treated with H_2S. A heavy precipitate of As_2S_3 came down.

Conclusion.—When As_2S_3 is boiled in the presence of SnS with a NaOH solution, part of the As is reduced to the metallic condition (brownish black residue, above) which remains after treatment with strong HCl, but is readily soluble in strong HNO_3.

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[1] Similar results were obtained with potassium hydroxide.

[2] 100 cc. of the caustic soda solution contained 20 g. solid NaOH.

[3] The complete insolubility of the sulfides was proved in every case by the negative tests obtained in the concentrated filtrates.

[4] See note under Test Experiment V. Similar residues were obtained here.

2. 300 mg. Sb, as $SbCl_3$, and 200 mg. Sn, as $SnCl_2$, were precipitated with H_2S; after boiling the precipitated sulfides with NaOH, as above, a large black residue remained. The filtrate was tested for Sb and Sn with decided positive results. The residue, after washing with dilute HCl, was boiled with concentrated HCl and filtered. The filtrate gave a good test for Sn. The residue immediately dissolved in strong HNO_3 with the evolution of oxides of nitrogen. On long boiling a white precipitate came down, which on dissolving in tartaric acid, and treating with H_2S gave a heavy orange colored precipitate of Sb_2S_3.

Conclusion.—When a mixture of Sb_2S_3 and SnS is boiled with a solution of NaOH, part of the Sb_2S_3 is reduced to black metallic Sb.

3. In order to ascertain whether the reduction of the As_2S_3 and Sb_2S_3 was due to the action of the Na_2SnO_2, which is one of the substances formed when SnS dissolves in NaOH($2SnS + 4NaOH = Na_2SnO_2 + Na_2SnS_2 + 2H_2O$), some precipitated As_2S_3 was dissolved in NaOH solution. To the clear solution was added a freshly prepared solution of Na_2SnO_2 and the mixture was heated. A brownish flocculent precipitate and metallic mirror soon formed. The solution was filtered; the residue was boiled with strong HCl and then filtered. The residue from this treatment was dissolved in HNO_3, reduced with SO_2, and treated with H_2S. A heavy lemon colored precipitate was As_2S_3.

4. Likewise, when a solution of Sb_2S_3 in NaOH was treated with a solution of Na_2SnO_2, a black flocculent precipitate and metallic mirror formed. This precipitate was shown to be Sb.

Thus the objections to the use of NaOH, as a reagent for separating the copper and tin groups, are:

a. SnS is not regularly dissolved by NaOH.

b. In the presence of SnS, the sulfides of As and Sb when treated with a solution of NaOH are partly reduced and metallic As and Sb are precipitated. Experiments performed with KOH gave similar results.

II.

The Action of a Mixture of NaOH and H_2O_2 on the Sulfides of Group 2.—Since the above experiments showed that the separation of the divisions of Group 2 by means of NaOH is rendered incomplete by the insolubility of SnS therein, the following experiments were carried out in order to determine the effect of using a solution of H_2O_2 in conjunction with the NaOH, the purpose of the H_2O_2 being to oxidize the SnS. Separate solutions, each containing 500 mg. of one of the metals of Group 2, were completely precipitated with H_2S, washed, filtered, and boiled for 2 minutes with a mixture of 25 cc. of a 20% solution of NaOH and 20 cc. of a 3% H_2O_2 solution. The sulfides of Hg and Cd were completely insoluble. PbS, CuS, Bi_2S_3, were partly soluble. As_2S_3, SnS and SnS_2 were practically completely soluble[1], while Sb_2S_3 was found to be only partly soluble.

Sb_2S_3.—When 500 mg. of Sb, precipitated as Sb_2S_3, were treated with NaOH and H_2O_2 a large white precipitate immediately came down.

PbS.—When 50 mg. of Pb precipitated as PbS, were treated as above, the black precipitate became white and then dissolved completely. (H_2O_2 oxidizes the PbS to $PbSO_4$ which dissolves in NaOH.) However, when a few bubbles of H_2S were passed into the solution, the Pb was completely precipitated.

CuS.—On adding NaOH and H_2O_2 to 500 mg. Cu, as freshly precipitated CuS, the latter was converted to a beautiful blue granular substance.[2] The mixture was boiled for 2 minutes, diluted and filtered. The filtrate possessed a light blue color;

[1] See note under Test Experiment V. Similar residues were obtained here.

[2] The composition of these precipitates is being investigated.

on treating it with a little H_2S, a black precipitate of CuS was thrown down. The filtrate from this treatment was no longer blue and gave a negative test for Cu.

Bi_2S_3.—On the addition of NaOH and H_2O_2 to 500 mg. Bi as Bi_2S_3, the latter, a dark brown flocky precipitate, was converted into a very light brown granular substance.[1] The mixture was boiled for 2 minutes, diluted, and filtered. A little H_2S was then passed into the clear filtrate; a dark brown precipitate of Bi_2S_3 came down. The filtrate from this second precipitation gave a negative test for Bi.

Conclusion.—NaOH and H_2O_2 cannot be used for separating the divisions of Group 2, because the sulfide of Sb is only partly dissolved, the remainder coming down as a white precipitate (probably the metantimonate of Na).

III.

The Action of a Mixture of KOH and H_2O_2 on the Sulfides of Group 2.—Since the partial insolubility of the Sb_2S_3 in NaOH and H_2O_2 was due most likely to the formation of the metantimonate of Na, which is not very soluble, it occurred to the authors to substitute KOH for NaOH, inasmuch as the corresponding potassium compound is known to be soluble.

Separate solutions, each containing 500 mg. of one of the metals of Group 2, were completely precipitated with H_2S, washed, filtered, and boiled for 2 minutes with 25 cc. 25% KOH and 20 cc. 3% H_2O_2 solutions. HgS and CdS were completely insoluble. The sulfides of Pb, Cu and Bi were partly soluble. As_2S_3, Sb_2S_3, SnS, SnS_2 were practically[2] completely soluble.

The sulfides of Pb, Cu and Bi were acted upon by KOH and H_2O_2 in the same manner as by NaOH and H_2O_2. When H_2S was led into the alkaline solution, the PbS was completely reprecipitated by a few bubbles of H_2S; but the CuS and Bi_2S_3 required much more H_2S for their reprecipitation.

When H_2S was led into the KOH solution containing H_2O_2, and the solution was then acidified, a heavy precipitate of sulfur came down (the acid liberating H_2S from reaction with the K_2S, and the H_2S being oxidized to S by the H_2O_2).

Conclusions.—(*a*) A mixture of KOH and H_2O_2[3] when used to separate the sulfides of Group 2 possesses the disadvantage in requiring the prolonged treatment of the alkaline solution with H_2S for the purpose of rendering the CuS and Bi_2S_3 completely insoluble.

(*b*) The method has the further objection in yielding a precipitate of S when the alkaline solution, after treatment with H_2S for the reasons stated above, is acidified with HCl.

IV.

Oxidation of the Solution Containing the Metals of Group 2 by Means of H_2O_2, before Precipitating with H_2S, and Treatment of the Precipitated Sulfides with KOH.—Since the preceding experiments showed that it is not feasible to oxidize stannous tin, when it is in the form of SnS, the following experiments were performed in order to determine whether oxidizing the stannous tin while in solution (before precipitation with H_2S) would be more desirable:

Separate 25 cc. solutions, each containing 500 mg. of one of the metals of Group 2, were neutralized with NH_4OH and reacidified with 10 cc. HCl (1.19). 10 cc. of 3% H_2O_2 were then added and the mixture boiled down with stirring, to one-half this volume.[4] The solutions thus freed of the excess H_2O_2 were then neutralized with NH_4OH, reacidified with 2.5 cc. concentrated HCl and H_2S passed in until precipitation was complete. The precipitated sulfides were then boiled for 2 minutes with 25 cc. of a 25% KOH solution. The sulfides of As, Sb, stannic and stannous Sn were practically[1] completely soluble. The sulfides of Hg, Cu, Bi and Cd were completely insoluble. PbS dissolved to a very small extent, but was completely reprecipitated on treating the alkaline solution with a little H_2S.

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[1] The composition of these precipitates is being investigated.

[2] See note under Test Experiment V. Similar residues were obtained here.

[3] No better results could be obtained by substituting Br water for H_2O_2.

[4] When 500 mg. of Sb, as $SbCl_3$, are oxidized by H_2O_2, the concentration of acid necessary to hold the Sb in solution is 9 cc. HCl (1.19) in a volume of 50 cc. The

As_2S_5.—The action of H_2O_2 on the As in solution is to oxidize it to the pentavalent condition with the result that its subsequent complete precipitation with H_2S, as is well known, is rendered very difficult.

500 mg. As, as a HCl solution of As_2O_3 were treated with H_2O_2 as given above, and then treated with a stream of H_2S for one-half hour in a hot solution containing 2.5 cc. HCl (1.19) in a volume of 40 cc.; it was found that a relatively large proportion of the arsenic had not been precipitated.

Conclusion.—While the preliminary oxidation of the solution containing the metals of Group 2 by H_2O_2 is advantageous, inasmuch as the stannous tin is thereby oxidized, it is undesirable because the As is oxidized at the same time to the pentavalent condition, in which state its subsequent precipitation with H_2S becomes a long and tedious process.

V.

Treatment of the Solution Containing the Metals of Group 2 with SO_2, Followed by the Addition of KOH to the Precipitated Sulfides.—The following experiments were performed in order to determine whether SO_2 could be used to oxidize stannous tin while in solution (before precipitation with H_2S):

Separate 25 cc. portions, each containing 500 mg. of one of the metals of Group 2, were neutralized with NH_4OH and reacidified with 5 cc. HCl (1.19). 75 cc. of a saturated solution of SO_2 were added and the resulting solution warmed for 25 minutes. After boiling down to one-half its volume to drive off the excess of SO_2, the solution was neutralized with NH_4OH and 2.5 cc. HCl (1.19) were added. H_2S was then passed into the solution for several minutes and again after dilution to 120 cc. until precipitation was complete. The precipitated sulfide, after filtering, was in each case boiled for 2 minutes with 25 cc. 25% KOH. The result of this treatment showed that the sulfides of Hg, Cu, Bi and Cd were completely undissolved. PbS dissolved to a small extent but was completely precipitated with a little H_2S. The sulfides of As, Sb and Sn were practically completely dissolved.[2]

Conclusion.—From the above experiments it is evident that by using SO_2 to oxidize stannous tin, KOH may be used to separate the sulfides of the divisions of Group 2. The use of SO_2 has the added advantage of reducing pentavalent As at the same time.

VI.

Formation of K_2S when a Tin Group Sulfide is Treated with KOH.—A mixture of 500 mg. Sb, as $SbCl_3$, and 10 mg. Pb, as $Pb(NO_3)_2$, was completely precipitated with H_2S, filtered, washed and then boiled for 1 minute with 25 cc. 25% KOH. The mix-

solution was boiled down to half its volume in order to decompose the excess H_2O_2 which would otherwise have given a precipitate of S with the H_2S subsequently added

[1] See note under Test Experiment V. Similar residues were obtained here.

[2] A very slight residue remained on the filter when 500 mg. of As, Sb or Sn in the form of sulfides were dissolved by the KOH and the resulting solution filtered. The residues from the As and Sn(ic) solutions were no more than a smudge on the filter. The residues from the Sb and Sn(ous) solutions were more noticeable than these; but still could leave no doubt as to the absence of a significant amount of a metal of the Cu group. When diminishing amounts of the metals (400, 300 mg., etc.) were taken, the residues became more and more unnoticeable.

ture was diluted with 35 cc. water and filtered; a black residue was obtained. The perfectly clear filtrate was then treated with H_2S. No precipitation or coloration formed, showing that the PbS was completely undissolved by the KOH because of the presence of K_2S derived from the solution of Sb_2S_3 in the excess of KOH.[1] The experiment was repeated with mixtures of 500 mg. As, as an HCl solution of As_2O_3, and 5 mg. Pb, as $Pb(NO_3)_2$, and with 500 mg. Sn, as $SnCl_4$, and 50 mg. Pb, respectively. The same results were obtained. Therefore, in the presence of a relatively large amount of a Sn group sulfide, the treatment of the KOH solution with H_2S in the procedure may be dispensed with. Further evidence of the formation of K_2S is supplied in Test Experiment 7.

VII.

The Action of H_2O_2 in Reprecipitating HgS from the KOH Solution.—It was found that more or less HgS always passed into the alkaline filtrate with the sulfides of the tin group because of the presence of K_2S in the solution. In the following experiments a method has been adopted for completely reprecipitating the HgS without bringing down any of the Sn group metals:

A mixture of 25 mg. Hg, as $Hg(NO_3)_2$, and 500 mg. As, as a HCl solution of As_2O_3 was completely precipitated with H_2S. The mixed sulfides, after washing, were boiled for 2 minutes in 25 cc. of a 25% KOH solution; the precipitate completely dissolved to a clear solution. The solution was diluted with 35 cc. of water and treated with a few bubbles of H_2S; it still remained clear. 30 cc. 3% H_2O_2 were then added and the mixture was boiled for one minute. A black precipitate came down. The mixture was boiled for one minute longer and filtered. The residue gave a positive test for Hg. The filtrate was concentrated to one-half its volume in order to oxidize the As_2S_3 to arsenic acid and to decompose the excess H_2O_2; it was then acidified with HCl. No precipitate of any kind came down, thus showing the HgS to have been completely precipitated by the H_2O_2.

When 1 mg. Hg, as $Hg(NO_3)_2$, was treated with 500 mg. Sn, as $SnCl_4$, as above, on the addition of the H_2O_2 to the alkaline solution, the HgS was completely reprecipitated and a good confirmatory test with $SnCl_2$ was obtained.

To test the method the following test analyses were used:

TEST ANALYSES.

Solution.	Hg.	Pb.	Cu.	Bi.	Cd.	As(ous).	As(ic).	Sb(ous).	Sn(ous).	Sn(ic).
1.......	1	.	...	.	...	1	...	500	1	...
2.......	...	.	...	.	...	1	...	1	500	...
3.......	...	1	...	1	2	500	...	...	...	...
4.......	...	.	...	.	500	...	...	...	1	...
5.......	...	.	...	.	...	1	...	1	500	...
6.......	500	2	...	.	1	...	...	...	...	...
7.......	1	.	250	.	...	...	...	...	...	250
8.......	1	2	500	.	...	...	...	...	...	1
9.......	...	.	...	.	...	1	...	500	...	2
10.......	...	.	...	.	..	2	...	2	500	...
11.......	1	.	500	.	...	...	...	...	...	...
12.......	...	.	1	.	...	...	...	500	...	1
13.......	1	.	...	.	...	...	500	...	...	...

The results of the above analyses were all successful. 1 mg. of arsenic was always detected by using the $(NH_4)_2MoO_4$ confirmatory test.

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[1] See Test Experiments 1 and 5, showing the solubility of PbS in KOH.

In analyses Nos. 2, 5, 9 and 10, very slight residues[1] were left on the filter after treatment of the precipitated sulfides with KOH, but in no case was the size of the residue such as to indicate the presence of significant amounts of metals of the Cu groups.

Summary.

1. The well-known objectionable features of the ammonium polysulfide method for the separation of the copper and tin groups have led to many attempts to replace it by a more suitable process; of these the sodium carbonate, sodium hydroxide, and potassium hydroxide methods taken alone or in conjunction with hydrogen peroxide are the best known. These have been examined and their shortcomings pointed out.

2. A scheme of analysis has been devised which overcomes the chief difficulties in the analysis of the filtrate of Group 1. The chief features of the method are:

(*a*) The preliminary precipitation of the alkaline earth metals together with some of the lead before precipitation of Group 2 with hydrogen sulfide

(*b*) Treatment of the filtrate from the precipitation of the alkaline earth metals with sulfur dioxide before passing in hydrogen sulfide, in order to oxidize stannous tin and to reduce pentavalent arsenic.

(*c*) The complete separation of the sulfides of the divisions of Group 2 by means of potassium hydroxide.

3. The results of a number of test analyses show the method to be trustworthy.

NEW YORK, N. Y.

EQUILIBRIA IN THE SYSTEMS, WATER, ACETONE AND INORGANIC SALTS.

BY GEO. B. FRANKFORTER AND LILLIAN COHEN.

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Introduction.

The dehydration of acetone is very similar to that of alcohol and ether. In most cases where dehydration of organic liquids takes place, the phenomenon of the formation of two definite layers also takes place. The salts most commonly used for dehydration purposes are CaO, $CuSO_4$, $CaCl_2$, K_2CO_3, Na_2SO_4, $MgSO_4$, $CaSO_4$, and KCl. $CaCl_2$ offers disadvantages inasmuch as it frequently forms compounds with the liquids and cannot be used in drying them. The only experiments of value on the efficiency of these drying agents were made by Siebenrock[2] in the drying of ether; Foote and Scholes[1] in the drying of alcohol; and Frankforter and Frary[2] in the drying of alcohol.

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[1] See note under Test Experiment 5.

[2] *Monatsh.*, 30, 759–66.

Frankforter and Frary[2] showed that anhydrous potassium fluoride is in the same class as anhydrous potassium carbonate and that its hydrate is more efficient than the hydrated carbonate.

In the dehydration of acetone containing water, it was noticed that two layers were formed when a sufficient quantity of a salt, such as $CaCl_2$, KF, K_2CO_3 or NaCl, was added. Linebarger,[3] Snell,[4] Bell,[5] McElroy and Krug,[6] Timmermans,[7] and Herz and Knoch[8] made investigations on the influence of various salts causing the formation of layers in aqueous solutions of acetone. In 1912, Frankforter and Frary obtained layers in aqueous solutions of ethyl and propyl alcohols with potassium fluoride. Since the potassium fluoride was found to be so effective in salting out the two alcohols, a study was made of its action with aqueous solutions of acetone. A saturated solution of potassium fluoride was added to a solution of acetone in water. A distinct separation into layers took place immediately.

A study of the equilibrium in this system at the ordinary room temperature was undertaken. In connection with this, a study was made of the systems containing potassium carbonate, water and acetone; calcium chloride, water and acetone; and sodium chloride, water and acetone.

Theory.

The theoretical side of systems containing three components, which can have two liquid and one solid phase. has been the subject of a series of investigations by F. A. Schreinemakers.[9] Application of the general principles has been made to the systems under discussion. In these systems we have the following conditions; (1) two liquids which are miscible in all proportions, and which in the absence of a third substance do not form layers under any conditions, (2) a salt which is soluble in the water, but not in the organic liquid (or the amount of the salt which dissolves in the organic liquid is practically negligible). This salt does not cause layer formation when added to any one of the two components in the absence of the other. The phases possible under these conditions are: (1) a homogeneous mixture of all three components, (2) two liquid phases, (3) a solid and two liquid phases, (4) a solid phase and one liquid phase. In case the hydrate is formed (4) represents two solid phases and one liquid phase. The graphic representation of these systems is the same as that given by Schreinemakers[1] and Frankforter and Frary.[2]

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[1] This Journal, 33, 1309.

[2] *J. Phys. Chem.*, 17, 402.

[3] *Am. Chem. J.*, 14, 380.

[4] *J. Phys. Chem.*, 2, 458.

[5] *Ibid.*, 9, 531.

[6] *J. Anal. and App. Chem.*, 6, 153.

[7] *Z. physik. Chem.*, 58, 129–213.

[8] *Z. anorg. Chem.*, 41, 318.

[9] *Z. physik. Chem.*, 22, 93, 515; 23, 417, 649; 59, 647.

Experimental.

The following determinations were made in all the systems studied:

1. Solubility of the salts in various concentrations of aqueous acetone, ranging from 95 to 100% acetone.
2. The binodal curve.
3. Tie lines.
4. Approximate positions of the plait point.
5. Quadruple points.
6. Some temperature effects.

Solubility.—In the determination of (1) the method used was not always satisfactory. In all cases except that of calcium chloride, the salt was carefully heated to a dull red heat for about ten minutes, then it was partially cooled in a desiccator and added, while still warm, to the different acetone water solutions.

The acetone solutions ranged in concentration from 95 to 100% and were made by carefully weighing the water in an Erlenmeyer flask provided with a ground glass stopper. The volume of acetone needed for a given concentration was carefully calculated from the specific gravity. This was added to the water and the contents of the flask were again weighed, giving the actual weight of acetone and water present. After the salts had been added to the solutions, the mixtures were heated to about 35-40°. The solutions remained in intimate contact with the salt for periods ranging from one week to ten days. Incidentally, as all the experimental work was done at 20°, the room temperature was kept as near 20° as possible. It ranged at times from 18° to 26°. In the case of sodium chloride the period of contact was much shorter. The salt solutions were shaken from time to time. The source of error in this method was due to the fact that if not enough salt was added the solution would not be saturated, and, if too much salt was added, the solution separated into two layers, giving entirely different concentrations of acetone than the ones under investigation. After standing for a given time, the solutions were decanted off and weighed quantities of the solutions were transferred to weighed platinum dishes and evaporated to dryness over water baths or on the radiator. The residue was weighable only in the case of calcium chloride; in all other cases it was negligible. The solubility of the salts in water was not determined, but the following solubilities were used: 92.3 g. of potassium fluoride are soluble in 100 g. of water; but this is an inconvenient form, the percentage of the anhydrous salt in 100 g. of the saturated solution being more convenient to work with. This is equivalent to 48% of anhydrous salt.[1] The solubility of potassium carbonate is 112 g. of the anhydrous salt in 100 g. of water at 20°, or 53.06% carbonate. For calcium chloride the solubility used is that given by Roozeboom[2] (74.5 g. of $CaCl_2$ in 100 g. of water, which is equal to 42.69 g. of $CaCl_2$ in 100 g. of the solution). The solubility of NaCl used was 35.79 g. in 100 g. of water or 26.35% of the solution as sodium chloride. The following method was employed in determining the binodal curve: An Erlenmeyer flask of about 400 cc. capacity, provided with a carefully ground glass stopper, was used in all the determinations. A side neck was blown into the flask at such an angle that a short thermometer could be inserted into the neck by means of very thin rubber cork, thus allowing the bulb of the thermometer to be constantly immersed in the solution. The thermometer was calibrated by comparison with a standard certified thermometer. The flask was carefully dried and weighed. The salt that was to be used, except in case of the calcium chloride, was heated to red heat for about ten minutes, cooled in a desiccator, rapidly transferred to the weighed flask and weighed immediately. Water from the buret was added, all the salt was completely dissolved and the flask with water was again weighed. The difference in the last two weights showed the amount of water. The indicator was then added. As it was difficult to see the appearance and the disappearance of two phases, the same indicators used by Frankforter and Frary were again used, spirit blue for all the systems except the potassium carbonate. In the carbonate system, on account of the bleaching action of the alkaline solution on the spirit blue, solid particles of phenolphthalein were used. In all cases precautions were taken not to use too much of the indicator, because with excess of the indicator the end point would be more obscure than if no indicator at all were added.

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[1] *Z. physik. Chem.*, **59**, 647.

[2] *J. Phys. Chem.*, **17**, 402.

Bonner[3] is the only other investigator of binodal curves who introduced an indicator, making use of small quantities of lamp black. The colored indicator is more convenient than the lamp black indicator.

After the addition of the indicator, a very small quantity of acetone was added. If two layers did not appear more acetone was added until there was a second definite layer present. The additional acetone was then weighed and water was carefully added from the buret until the two layers just became homogenous. The water was added very carefully and the contents of the flask were thoroughly shaken and allowed to stand; otherwise too much water would be used, nullifying results. The additional water was weighed, and more acetone was added to form

[1] *Ber.*, 39, 1716.

[2] *Z. physik. Chem.*, 4, 31.

[3] *J. Phys. Chem.*, 14, 738.

a second layer. This was weighed and water added as before until the second layer just disappeared. Series of determinations were made, starting out with saturated salt solutions, continuously adding water and acetone until the flask would hold no more of the solution.

The temperature changes of a few degrees around 20° were very noticeable in the system of calcium chloride. They were less marked in the case of potassium fluoride, and with certain concentrations, were not at all noticeable with potassium carbonate. In changing the temperature from 5° to 40° in the latter system, no particular effect was noticed in determining points on the binodal curve. This can also be seen in Fig. 3, where the points determined by Bell[1] are plotted beside the binodal curve obtained at 20°. Bell's results are for an isotherm at 25°. In determining points on the binodal curve the phenomenon of "foam building" mentioned by Ostwald was noted. According to Ostwald all aqueous solutions above their saturation temperatures are inclined to form foams, no foams being found in heterogeneous mixtures. When the solutions containing two layers were shaken the bubbles quickly disappeared, but on the immediate formation of a single layer the foam was easily obtained.

Tie Lines.—The binodal curve is, then, the locus of all saturated homogeneous liquids, the effect of adding a particle of salt causing the formation of two layers. The composition of these two layers can then be determined and tie lines drawn. The tie lines are not necessarily parallel, though the tendency toward this is noted in lines near the plait point. The composition of these two solutions, which are called conjugate solutions, was determined in the following manner: The solutions were transferred to a separatory funnel, the upper and lower liquids separated and weighed portions of each evaporated to dryness. This gave the amount of salt in the upper and lower layers, respectively. By reference to the tables for the different binodal curves, the percentage composition of the two solutions can be easily determined. A straight line drawn between these two points on the binodal curve representing the conjugate solutions is called the "tie line."

Plait Point.—Difficulty was experienced in determining some of the plait points, because as the solutions have more nearly the same composition, their densities approach each other in value and the layers, while they do form, do not separate out so quickly, one solution being held in fine suspension in the other. Instead of determining the plait point directly several tie lines were located, and by interpolation the plait point was determined. It could have been determined directly.

Quadruple Points.—These were determined by the following methods: A saturated aqueous solution of the salt was made and acetone was added until two very distinct layers appeared, the volume of each being equal to at least three hundred cubic centimeters. Additional salt was then added, and the flask was warmed to get more of the salt into the solution. The flask and contents were then cooled to 20° and in most cases crystals of the hydrate appeared in a very short time. The solutions were kept in contact with each other for periods exceeding a week, and the contents of the flask were shaken at frequent intervals. In some instances a shaking machine was used. Weighed portions of both the upper and lower layers were transferred to weighed platinum dishes and the contents of the dishes evaporated to dryness. Their salt content was thus determined and expressed in grams per hundred grams of the solution. In determining the acetone content of the upper layer, the solution was distilled and the distillate collected in a Will-Varrentrapp apparatus which was kept cold with salt and ice. This prevented the rapid evaporation of the acetone. The contents of the distilling flask were distilled to dryness. The specific gravity of the acetone is then determined, and from the table given by McElroy and Krug[1] the amount of acetone present is obtained. Another method that might be used would be to make up a series of solutions, with varying water and acetone content, saturate them with the given salt and determine the specific gravities of the solutions. The series of specific gravities could be plotted and used as standards of comparison. The same method could be used in determining the exact composition of the lower layers, but difficulties are encountered in determining the acetone content. When salts such as potassium fluoride or carbonate were used the amount of acetone in the lower layer was slight. Therefore, very large quantities of the lower layers had to be used. In determining the acetone content, 200–400 g. of the solution were transferred to a weighed flask, weighed and then placed in a distilling flask, and water was added to lower the density of the solution. The contents of the flask were then distilled over into either a weighed flask or Will-Varrentrapp bulbs, which were kept cool by salt and ice. To be sure that all the acetone had passed over, the distillation was always continued from five to ten minutes after the thermometer registered from 98–100°. If the volume of the distillate was not sufficient for specific gravity determinations, more distilled water was added. It was not desirable to add much water as the acetone content was not high. The distillate was weighed and the specific gravity determined; from the tables the amount, by weight, of acetone present in the distillate found, and from this was obtained the amount of acetone present in the original amount of solution taken. Concrete illustrations are given in the various systems studied. The data at hand were then; the concentration of acetone in the water and salt solution, and the amount of salt present.

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[1] *J. Phys. Chem.*, 9, 537.

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[1] *J. Anal. and App. Chem.*, 6, 187, (1892).

A second quadruple point was determined when the salt used formed a hydrate. This point determined the dehydrating power of the anhydrous salt. To an aqueous solution of acetone, such as the one from the distillate of the upper of the first quadruple point, excess of the anhydrous salt was added. After the flask was warmed and then cooled, part of the salt appeared as the hydrate and part was still anhydrous. There were four phases present, hydrate, anhydrous salt, one liquid phase and the vapor. The temperature was fixed, so the system was invariant. The acetone content of the liquid phase was determined in the same manner as the acetone content of the upper layer of the first quadruple point. The solution was decanted off from the solid salt and distilled to dryness. The % of acetone present in the distillate was obtained by determining its specific gravity. The amount of salt present in the liquid layer was determined by the evaporation of a weighed quantity of the solution, and the weight of the residue was obtained. Traces of the salt were found only in the case of calcium chloride. With the carbonate and fluoride practically nothing was left in the dish after evaporation.

Temperature Effects.—In determining points on the binodal curve for all the systems, the temperature was kept at 20°. The changes produced by variations in temperatures were not so marked in dilute solutions as in concentrated solutions of the various salts. Absolute determinations of the upper and lower critical solutions temperature were not made. Homogeneous solutions of the salts in water and acetone were made at temperatures as low as 5° and the solutions were gradually warmed through 5°, and if clouding took place water was added until the cloud disappeared. The excess of water was then weighed. Heat was again applied, and the change produced by the next 5° was noted. The process was repeated until temperatures of 40° were reached.

Materials.

Calcium Chloride.—The calcium chloride used was Merck's purified especially for analytical purposes. Five grams of the calcium chloride dissolved in 25 cc. of water did not give a clear solution and the solution was slightly alkaline. Even though the slight amount of calcium oxide present might not affect the experimental data, the cloudiness of the solution would interfere with end point determinations of positions on the binodal curve. The alkalinity was removed by a process described a little farther on. The salt was found to be pure according to tests given by Krauch.[1] The calcium chloride contained some water. When calcium chloride containing one molecule of water is heated, hydrochloric acid is given off and the basic salt is formed.[2] To prevent the formation of the oxychloride and to remove the water, the following methods were used:

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[1] Testing of Chemical Reagents

[2] M. Dennstedt, *Ber.*, 1, 602.

The calcium chloride was fused and, while in a state of fusion, a current of dry hydrochloric acid gas was introduced. The fused salt was then cooled in a desiccator and was ready for use. It was difficult to prepare large quantities of calcium chloride by this method. It was therefore discarded and the following one substituted in the preparation of all the calcium chloride used: A hydrochloric acid generator was connected with a drying bottle containing concentrated sulfuric acid and then to two calcium chloride drying towers. From the last drying tower a delivery tube was placed in an Erlenmeyer flask, which was immersed to the neck in a porcelain air bath. The calcium chloride was powdered and 250–300 g. were placed in the flask, the temperature of the air bath ranging from 160 to 220°. The hydrochloric acid gas was passed into the heated chloride, which was stirred frequently to insure contact of the gas with all of the chloride. At the end of an hour no more moisture formed in the neck of the flask. The chloride was then heated two or three hours longer, the heat was removed and the generation of the gas was stopped. When the contents of the flask were cooled to 100°, the chloride was transferred to a desiccator containing pumice stone well sprinkled with phosphorus pentoxide. The salt, when dissolved and tested with phenolphthalein, gave a neutral reaction. A solution containing over 2 g. of this salt turned pink when one drop of $N/10$ sodium hydroxide solution was added.

The requirements of the experiments did not demand calcium chloride of the purity used by Richards and Honigschmid[1] in their atomic weight determination of calcium.

Potassium Fluoride.—This salt was labeled "Merck's chemically pure potassium fluoride." If gave an acid reaction. The acidity was removed when the salt was heated to red heat, all the excess hydrofluoric acid being driven off. The potassium fluoride did not dissolve completely in water before it was heated, the solution being cloudy. After the salt had been heated the aqueous solution was clear, indicating that the original salt contained free acid which attacked the glass.

Potassium Carbonate.—Pure potassium carbonate was not available, so the salt was made from the bicarbonate. The bicarbonate was dissolved in boiling water, boiled for half an hour, the boiling solution cooled, and the crystals that separated out were dried by suction. The object of boiling was to convert some of the salt into the carbonate. The salt was dried several hours in an electric drying oven at 160°. As complete decomposition takes place at 190°, the salt was then transferred to a platinum dish and heated to red heat until the excess of carbon dioxide and water had passed off. The temperature was kept below fusion to prevent the formation of potassium hydroxide and the loss of carbon dioxide.[1] The potassium carbonate was always reheated and cooled in the desiccator before being used for determinations.

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[1] THIS JOURNAL, 33, 28.

Sodium Chloride.—Kahlbaum's chemically pure sodium chloride was used. Its solubility was 35.74 g. of salt in 100 g. of water. The salt was powdered and heated to red heat for a few minutes until all the "crackling" stopped. It was then cooled and used.

Methyl Alcohol.—Kahlbaum's absolute methyl alcohol, 100% pure, was used, specific gravity 0.79576, at 15.55°/4°, b. p. 64.6°.

Acetone and Its Purification.—The acetone was Kahlbaum's purest quality from the bisulfite compound. It was found to contain some water, in addition to very small quantities of other impurities. It was necessary to purify it before the salting out processes could be satisfactorily carried out. Fractional distillation failed to remove the last traces of impurities. Calcium chloride and potassium carbonate were tried, but were found unsatisfactory. Magnesium amalgam was next tried, with better results, but was abandoned on account of the loss of acetone during the process, as the amalgam held mechanically a considerable quantity of the acetone. Finally, sodium amalgam was used successfully, after the acetone had been first dried for some time with calcium chloride. So satisfactory was the sodium amalgam method that it was used later for preparing chemically pure acetone from the commercial product. The method of purification consisted in simply treating the acetone with calcium chloride, decanting off the dried acetone, treating it with sodium amalgam and finally decanting off the acetone and redistilling. The residue was reddish brown. The residue obtained by Bell's method of purification was yellow, which may have been due to decomposition, as it was found that acetone that had stood in the sunlight gradually turned yellow. This method of treatment gave strictly pure acetone even from the commercial product, hence practically all the material used in this work was prepared from the crude product by the above method.

R. Bacon and P. Freer[2] found that sodium reacted with acetone forming C_3H_5ONa, a white flocculent precipitate which turned red on exposure to the air. Whether the red color found in the residue, after the distillation of the acetone which had been treated with this sodium amalgam, is due to a sodium compound is not known, as the residual solution has not as yet been investigated The formation of this sodium compound is doubted by Taylor.[3]

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[1] Roscoe and Schorlemmer, 2, 351 (1907).

[2] *Philipp. J. Sci.*, 267, 76; through *C. A.*, 1, 1694.

[3] *J. Chem. Soc.*, 89, 1257.

PHYSICAL CONSTANTS.

Index of Refraction. Pulfrich refractometer (latest model). Temperature 20°.

Commercial acetone.........	H α 1.36309	H β 1.34882	H γ 1.33999
Purified acetone.............	H α 1.36213	H β 1.34834	H γ 1.339506
Kahlbaum's acetone, purified.	H α 1.36219	H β 1.34823	H γ 1.33943

Brühl[1] obtained the following results:

Acetone, sp. gr. 20°/4°......	0.7920		
	H α 1.35715	H β 1.36393	H γ 1.36780

The data given for the specific gravity and the boiling point of acetone by different investigators do not generally agree. The acetone used in this work had a boiling point of 56.3–4°.

Systems.

Potassium Fluoride Water and Acetone.—This system is one that has never been studied, because the usefulness of potassium fluoride has but recently been shown by Frankforter and Frary.[2] In 1912 they found that the addition of potassium fluoride to ethyl or propyl alcohol mixtures with water would cause the separation of the two miscible liquids into layers. The potassium fluoride salted out the alcohol. As a dehydrating agent the saturated solution of the hydrate of the fluoride was better than a saturated solution of the hydrate of potassium carbonate, owing to the lower vapor tension of the solution of the fluoride. Potassium carbonate hydrate removes more water than the hydrate of potassium fluoride There is a similarity in their action with acetone, though it is less noticeable with acetone than with alcohol The conduct of acetone and water with either potassium carbonate or fluoride is very similar to that of alcohol and water with the same salts. The fluoride is soluble to some extent in alcohol, 4.79 grams per hundred grams of the solvent. In acetone the fluoride is practically insoluble. The anhydrous fluoride was heated for about ten minutes, allowed to cool, and while still warm was added to the anhydrous acetone. The acetone was shaken from time to time, and after standing in the room at about 20° for over three days, the amount of the potassium fluoride in a known weight of the solution was determined by conversion of the potassium fluoride into the chloride, by addition of hydrochloric acid and subsequent evaporation. It was rather difficult to determine the solubility of the salt in the less concentrated solutions of acetone, because, if too much salt was added, the salt took up the water and two layers were formed. The acetone layers in no case gave any perceptible amount of potassium fluoride in the solution, and, in general, potassium fluoride can be classed as a salt that is insoluble in acetone. In the study of this system the two quadruple points, tie lines, binodal curve and the approximate plait points were determined A few experiments were made to show the temperature effect, within narrow ranges of temperature. The method used in determining the points on the binodal curve and the quadruple points has been already described. The data for the binodal curve are given in Table I and the positions of the other points are given in Fig. 1. The first quadruple point determined is the one where the hydrate, water, acetone and vapor are in equilibrium at 20°. According to the phase law, if the temperature is kept constant, the system is invariant and is in equilibrium. The composition of both layers was determined by the potassium fluoride and acetone content in both the upper and lower layers. When 20–30 g. of the upper solution were treated with hydrochloric acid, to prevent loss of the chloride, and the solution was evaporated to dryness, no appreciable residue was found. This indicated a potassium fluoride free upper layer. The rest of this upper layer was carefully distilled. A 150 cc. distilling flask was connected with a condenser and then to a Will-Varrentrapp "U" tube, which was kept in a freezing mixture of salt and ice. The latter was used to prevent the loss of any vapors of acetone, as acetone has a high coefficient of expansion. The contents of the flask were distilled to dryness and the distillate from the "U" bulb was transferred to an Erlenmeyer flask. The temperature at which the distillate passed over was practically 56° until over 5/6 of the solution had passed off, when the temperature rose rapidly to 85–90°. The last trace of the distillate came off at 98 100°. Several fractions were distilled and thoroughly mixed. One slight source of error is noticed at the end of the distillation, a very slight brown resin, which decomposes at a high temperature, is left behind.

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[1] *Z. physik. Chem.*, 22, 189, 409.

[2] *J. Phys. Chem.*, 17, 402.

The specific gravity of this distillate was then determined. McElroy and Krug[1] have determined the data for a table of specific gravities for acetone at 20°/4°. In this table the specific gravities of 20 mixtures of acetone and water, ranging from zero to 100% of acetone, are given. In order to determine intermediate points, this table was plotted, the rectangular coördinates giving percentages and specific gravities. From the diagram the percentage of any acetone solution could be obtained from its specific gravity.

In the determination of the specific gravity of the acetone obtained from the upper layer, 0.798 at 20° was obtained. This corresponds to 98% acetone. A saturated solution of potassium fluoride will, then, dehydrate acetone to the extent of 98%. The amount of potassium fluoride in the lower layer was next determined. 32.679 g. of the lower layer were transferred to a weighed platinum dish and sufficient concentrated hydrochloric acid was added to convert all the fluoride into the chloride. This is done to prevent the loss of hydrofluoric acid, as the salt hydrolyzes. 19.625 g. of potassium chloride were obtained, which is equivalent to 46.3 g. of potassium fluoride in 100 g. of the lower layer. The acetone content of the lower layer was not measurable according to the specific gravity tables of McElroy and Krug. 106 g. of this solution were placed in a distilling flask and distilled, and the temperature rose at once, remaining at about 100° for over ten minutes. The distillate was weighed and its specific gravity was determined and found to be 0.9994 at 20°/4°. This shows that only traces of the acetone are present.

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[1] *J. Anal. and App. Chem.*, 6, 187.

In determining the second quadruple point, where the anhydrous potassium fluoride, the hydrate $KF.2H_2O$, acetone layer and vapor are in equilibrium at 20°, the acetone from the previous determination was used. It was kept in contact with the hydrated fluoride and the anhydrous salt at room temperature for over a week. The flask was shaken from time to time to insure complete contact, the acetone was decanted off and several determinations of the specific gravity were made at 20°/20°, giving the value 0.7932, or 99.9% pure acetone. This would indicate that with potassium fluoride practically anhydrous acetone can be obtained. Landolt and Börnstein tables give the specific gravity of 100% acetone 20°/20° as 0.793.

In determining the plait point and the tie lines, a series of conjugate solutions were made and the potassium fluoride content of the upper and the lower layers determined.

		Amount of solution.	Grams KCl.	Grams KF in 100 g. of solution.
I.	Upper layer	45.98	0.0295	0.05
	Upper layer	39.37	0.03	0.059
	Lower layer	53.936	16.006	23.12
	Lower layer	55.81	16.64	13.23
II.	Upper layer	33.869	0.710	1.634
	Upper layer	32.5315	0.6818	1.633
	Lower layer	19.7548	2.744	10.94
	Lower layer	23.1605	3.25	10.94
III.	Upper layer	15.1210	0.1095	0.5642
	Lower layer	19.5975	3.717	14.78
IV.	Upper layer	19.933	0.86	3.36
	Lower layer	18.133	1.862	8.00

From these tie lines, the approximate position of the plait point was found.

Comparison of the carbonate with the fluoride curve shows that it was easier to obtain the plait point on the fluoride curve.

The Effect of Temperature.—In studying the system $CaCl_2.H_2O$ and acetone, it was noticed that the solution, just homogeneous at 20°, became cloudy when the temperature increased even one-half of a degree. With potassium fluoride, water, and acetone, this clouding effect was not so evident. The temperature effects within narrow limits were determined, and are discussed later on.

TABLE I.—FOR THE BINODAL CURVE OF POTASSIUM FLUORIDE WATER AND ACETONE AT 20°.

Solvent added.		Total wt. of subst. present.			Wt. of subst. present in 100 g. of soln.		
Water.	Acetone.	KF.	Water.	Acetone.	KF.	Water	Acetone.
50.615	30.361	4.9433	50.615	30.361	5.75	58.91	35.34
4.983	7.897	4.9433	55.598	38 258	5.00	56 28	38.72
11.634	18.237	4.9433	67.232	56.495	3.84	52.25	43.91
12.055	20.903	4.9433	79.287	77.398	3.06	49.05	47.89
9.453	18.358	4.9433	88.740	95.756	2.61	46.84	50.55
10.895	22.112	4.9433	99.635	117.868	2.22	44.79	52.99
79.847	12.346	16.206	79.847	12.346	14.95	73.66	11.39
20.224	12.778	16.206	100.071	25.122	11.46	70.77	17 77
18.888	16.476	16.206	118.959	41.598	9.17	67.30	23.53
15.445	17.761	16.206	134.404	59.359	7.72	64.01	28.27
7.695	11.415	16.206	142 099	70.774	7 07	62.03	30.90
10.230	12.490	16 206	152.329	83.264	6.43	60.50	33.07
33.194	47.528	1.1273	33.194	47 528	1.38	40.55	58.06
8.715	24.505	1.1273	41.909	72.033	0.979	36 42	62.60
11.254	36.286	1.1273	53.163	108.319	0.693	32.69	66.61
9.49	26.795	1.1273	62.653	135 114	0.57	31.50	67.93
44.520	78.942	1.114	44.520	78.942	0.89	35.74	63.36
5.980	18.618	1.114	50.50	97.56	0.75	33 84	65.41
7 708	25.30	1.114	58.208	122.860	0 61	31.95	67.44
8 66	32.572	1.114	66.868	155 432	0 5	29.92	69.58
44.591	1.163	18.163	44.591	1.163	28 42	69.76	1.82
5.686	0.972	18.163	50.277	2.135	25.74	71.24	3.02
9.038	1.651	18.163	59.213	3.786	22.35	72.99	4.66
6.77	1.514	18.163	66.085	5 300	20.28	73.80	5.90
5.843	1.675	18.163	71.928	6.975	18 71	74.10	7.19
10.420	3.844	18.163	82.348	10.819	16 31	73.97	9.72
23.100	12.003	18.163	105.448	22.822	12.40	72.01	15.59
46.814	0.282	24.1185	46.814	0.282	33 86	65.73	0.397
8.300	0.935	24.1185	55.114	1.217	29.97	68.54	1.50
25.178	3.747	24.1185	80.292	4.964	22.05	73.41	4.54
19.882	6.088	24.1185	100.174	11.052	17.82	74.01	8.16
23.044	9.741	24.1185	123.218	20.793	14.34	73.29	12.37
79.437	0.341	63.2847	79.437	0 341	44 24	55.52	0.240
45.205	1.542	63.2847	124.652	1.542	33.34	65.66	1.00
20.566	1.515	63.2847	145.218	3 398	29.86	68.54	1.60
42.104	5.630	63.2847	187.322	8.928	24 38	72.16	3.45

Fig. 1 gives a graphic representation of this system.

Potassium Carbonate, Water and Acetone.—That potassium carbonate forms two layers when added to an aqueous solution of acetone has been shown by Linebarger,[1] Snell[2] and Bell.[3]

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[1] *Ann. Chem. J.*, 14, 380.

[2] *J. Phys. Chem.*, 2, 457.

[3] *Ibid.*, 9, 531.

Linebarger's work, although classed as quantitative by Timmermans,[1] is very incomplete and merely shows that two layers are formed when the carbonate is added to the water and acetone. He made only ten determinations on the binodal curve, and these, he admits, are not very accurate. His measurements are also made on points of the curve that do not give any indication of the general direction of the curve and no tie lines are determined. The method he used in determining the points on the curve was to add varying quantities of organic liquid and water from a buret to a titrated solution of the carbonate, until just a drop of water would clear up the milkiness caused by a drop of acetone. The data obtained by Linebarger have been recalculated and tabulated in parts per 100 g. of the solution. These are given in Table II, while in Fig. 3 the points on the curve indicated by ° are those obtained by Linebarger. His results were obtained at 20°.

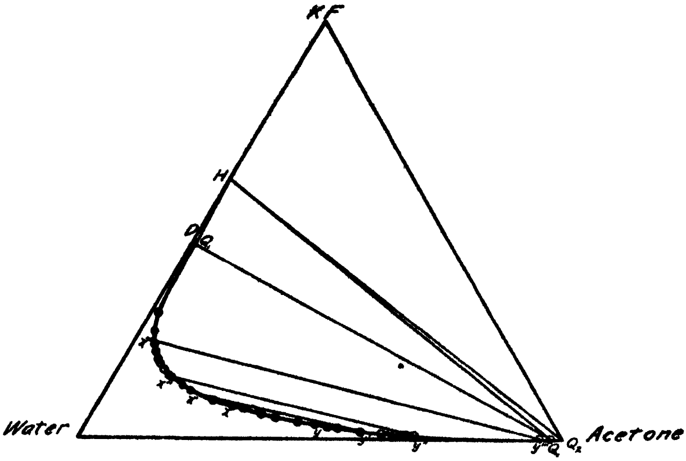

Fig. 1.—Equilibrium in the system: potassium fluoride, water and acetone.

TABLE II.

Temperature 20°.

K_2CO_3.	Acetone.	Water.	Total.	Per cent. K_2CO_3.	Per cent. acetone.	Per cent. water.
1	4.8	9.2	15.0	6.67	32.0	61.33
1	11.4	16.1	28.5	3.51	40.0	56.49
1	18.8	22.1	41.9	2.38	44.87	52.75
1	30.8	31.1	62.9	1.59	48.97	49.45
1	43.0	38.5	82.5	1.21	52.11	46.68
1	5.4	10.2	16.6	6.02	32.5	61.50
1	14.4	18.8	34.2	2.92	42.10	54.98
1	28.2	28.7	57.9	1.72	48.70	49.58
1	50.0	38.7	89.8	1.11	55.67	43.23
1	89.7	49.9	141.6	0.7	64.0	35.20

[1] *Z. physik. Chem.*, 58, 123.

These points fit in fairly well with the binodal curve, but when one considers the fact that the maximun amount of the carbonate used by Linebarger was 6.67 g. in 100 g. of the solution, and that a saturated solution contains over 53% of carbonate, the results cannot be considered very satisfactory, especially if one takes into consideration the dehydrating effect of potassium carbonate on acetone.

Bell determined points on the binodal curve over a much wider range, his concentrations of the carbonate varying from 2.34 g. in 100 g. of solution to 30.58 g. in 100, while the percentage of acetone decreased from 42.56 to 1.27. His particular object was not so much the determination of the points on the curve as to prove that the exponential expression of Bancroft,[1] $X^{\alpha}.y^{\beta}/z^{\alpha+\beta} = K$ would describe the equilibrium in the system, acetone, potassium carbonate and water. By simplification the above equation becomes $Z^{n}/_{y} = K$. Z denotes the grams of water, and y the grams of acetone per gram of salt. Bell tried to apply this equation to Linebarger's data, as well as to his own, and found that it could be applied neither to this system not to any system containing two consolute liquids and an electrolyte. Bell's data are obtained at 25° and are given in Table III and plotted in Fig. 3. The points are indicated by X. It is noticed

TABLE III.

Bell's data.			Recalculated in parts per 100 g.		
Grams K_2CO_3.	Grams H_2O.	Grams $(CH_3)_2CO$	K_2CO_3.	H_2O	$(CH_3)_2CO$.
1.456	34.41	26.36	2.34	55.30	42.36
1.924	35.67	23.64	3.14	58.26	38.61
2.257	35.57	21.49	3.80	62.4	33.8
2.251	36.10	19.494	3.89	62.41	33.70
2.746	37.92	20.645	4 48	61.83	33.69
2.694	39.94	19.153	4 36	64.64	31.0
3.016	37.87	19.510	4.99	63.43	31.57
3.380	39.25	19.001	5.48	63.68	30.83
3.984	40.13	17.303	6.5	65.45	28.05
4.571	42.89	17.426	7.04	66.10	26.86
4.981	42.81	16.173	7.79	66.93	25.28
6.022	45.17	14.602	9.2	68.5	22.2
7.349	45.0	11.078	11.58	70.95	17.47
8.093	49.91	12.339	11.51	70.95	17.54
9.06	50.05	10.246	13.06	72.17	14.77
9.765	50.17	8.940	14.17	72.84	12.98
11.076	49.99	6.802	16.32	73.66	10.02
12.396	50.87	5.572	18.01	73.9	8.09
14.509	50.4	3.656	21.16	73.51	5.33
15.744	51.03	2.966	22.57	73.17	4.26
7.82	50.53	2.143	25.28	71.68	3.04
19.67	50.48	1.563	27.43	70.4	2.17
22.602	50.38	0.940	30.58	68.17	1.27

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[1] *J. Phys. Chem.*, 1 34, 760.

that Linebarger's and Bell's data combined give a fair idea of the general character of this curve. Though Bell's data were obtained at 25°, they are compared with data obtained at 20°, because the temperature effect between these two points is not very marked. The method Bell employed in determining his points is very similar to the one used in this work. He controlled the temperature effect by the use of an Ostwald thermostat. He did not use any indicator in detecting the presence of the two liquid phases. With extreme concentrations he found difficulty in determining the end points. With extreme concentrations of carbonate in the water, where only traces of acetone were present, little trouble was found in distinguishing the vanishing point of the two layers, because the little globules of the second liquid phase took up enough of the indicator phenolphthalein to color them a dark violet. These globules formed on the surface, and, owing to surface tension, collected around the thermometer stem and the side of the flask, and when the contents of the flask were shaken, the globules were quickly set in motion and their presence readily detected. With concentrations exceeding 60% acetone and less than 0.5% potassium carbonate, the cloudiness was difficult to perceive, but by holding the flask to the sunlight the cloudiness was detected by transmitted light.

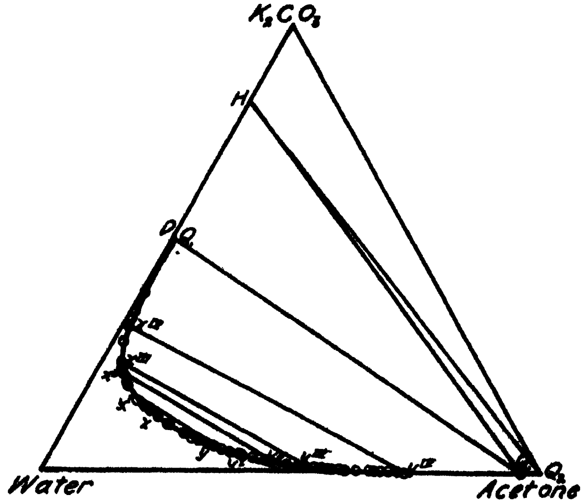

Fig. 2.—Equilibrium in the system: water, acetone and potassium carbonate.

In the system potassium carbonate, water, acetone, the points on the binodal curve given in Table IV were determined — two quadruple points, several tie lines, and, indirectly, the plait point. These are plotted on the triangular diagram of Fig. 2. Potassium carbonate was found to be practically insoluble in acetone, and was also found to be practically insoluble in solutions of 95–100% acetone. The determinations of the solubilities up to 92% are best obtained from the binodal curve.

In determining the tie lines, analyses of five sets of conjugate solutions gave the following results:

		Grams of solution.	K_2CO_3 found.	Total K_2CO_3 in 100 g.
I.	Upper layer	15.61	0.1111	0.7117
	Lower layer	24.268	5.9271	24.40
II.	Upper layer	15.85	0.0062	0.039
	Lower layer	24.627	8.0373	32.63
III.	Upper layer	73.29	0.9967	1.36
	Lower layer	57.43	13.1613	22.91
IV.	Upper layer	11.169	0.511	4.57
	Lower layer	14.939	2.534	16.92
V.	Upper layer	11.645	0.812	6.97
	Lower layer	12.315	1.819	14.77

A glance at Fig. 2 will show the position of the last tie line, relative to the curve, and the difficulty in obtaining the plait point. When the upper and lower layers have approximately the same composition and specific gravity, the two layers separate with difficulty. The plait point is then determined approximately. The plait point in the system potassium fluoride, acetone and water lies in a relatively different position on the curve and is more easily obtained. The calcium chloride, acetone, and water, tie lines are as difficult to obtain as the potassium carbonate. In determining the two quadruple points the method described in the potassium fluoride system was again used. The saturated solution of potassium carbonate was kept in contact with acetone and the hydrate of potassium carbonate for over a week. At the end of that period the solution was distilled, and the specific gravity of the distilled acetone was found to be 0.8037 at 20°/4°. Reference to the tables in use give an acetone content of 96.4%. 29.09 g. of the original solution of the upper layer gave a carbonate content of only 0.0007 g., or 0.0024 g. in 100 g. of solution. No attention is given to this result, as it practically coincides with the point of 100% acetone on the triangle.

Four hundred grams of the lower layer, which had a distinct acetone odor, were used to determine the amount of acetone in the lower layer, but, despite this large amount, it was not, ap-

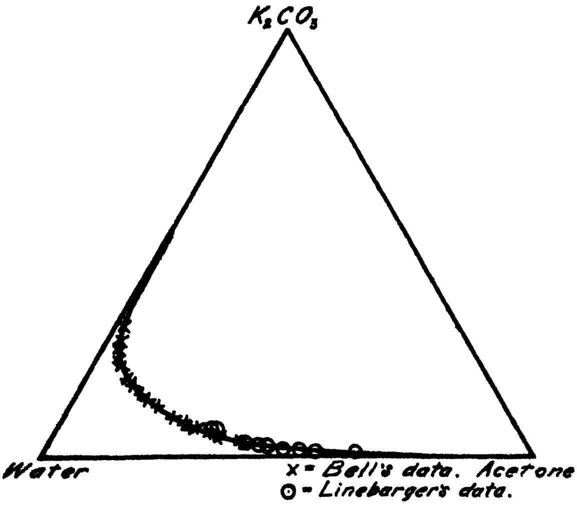

Fig. 3.

parently, possible to obtain enough acetone to determine the amount in the solution. The specific gravity of the weighed distillate from 400 g. of the solution was 0.9994, although acetone was present. In the reference tables, 0.9994 gives zero, or negligible quantities of acetone. In this solution, evaporation of 29.503 g. gave 15.4567 g. of K_2CO_3, which is equivalent to 52.38 g. of K_2CO_3 in 100 g. of the solution. This shows that at the quadruple point, the lower layer is nearly a saturated solution of potassium carbonate. Frankforter and Frary found the solubility of potassium carbonate to be 53.05 or 53.07 g. in 100 g. of the solution.

The second quadruple point was obtained in a manner similar to the second quadruple point of the fluoride system. The acetone which had been obtained from the distillation of the upper solution was added to anhydrous carbonate, and a little water was added to insure the formation of $2K_2CO_3.3H_2O$. More of the anhydrous salt was added until the four phases were formed, the two solid phases, hydrate and anhydrous salt, one liquid and one vapor phase. The contents of the flask were frequently shaken and were then decanted off and distilled to dryness. The specific gravity of the distillate at 20° was then determined. The acetone content was found to be only 98.3%. This acetone was again kept in contact with more of the anhydrous salt, and the hydrate and the solution were frequently stirred. At the end of the second week the distillation process was repeated and the acetone was found to be practically pure. The specific gravity found was 0.7933. This gives 99.8% acetone, thus anhydrous carbonate practically dries the acetone, but the time required for equilibrium to be reached is about twice that required with potassium fluoride. For this reason the fluoride is more satisfactory.

In determining some temperature effects in this system, it was found the temperatures between 5° and 40° had no effect on a solution which contained 2.7 g. potassium carbonate, 29.701 g. water and 12.95 g. of acetone. This solution was just homogeneous at 5°. It was then gradually warmed up to 40° and no effect and no cloudiness was noted.

Calcium Chloride, Water and Acetone.—Although calcium chloride is generally used in dehydrating acetone, the system that it forms with acetone and water has not been investigated. Snell[1] and Linebarger[1] merely note the fact that calcium chloride, as well as certain other chlorides, will produce two layers. The limits of the layers, binodal curves, etc., are not given. Calcium chloride is not very soluble in acetone. McElroy and Krug[1] classify calcium chloride among the salts that are very sparingly soluble. It was found that the average results of a series of determinations at 20° gave 0.02 g. of calcium chloride in 100 g. of

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[1] *Loc. cit.*

Table IV.

System Potassium Carbonate, Water and Acetone.

Solvent added.		Total wt. of subst. present.			Per cent. in 100 g. solution.		
Water.	Acetone.	K_2CO_3.	H_2O.	$(CH_3)_2CO$.	K_2CO_3.	H_2O.	Acetone.
55.107	5.971	14.189	55.107	5.971	18.84	73.22	7.94
20.984	10.344	14.189	76.091	16.315	13.32	71.38	15.30
8.29	5.063	14.189	84.381	21.378	11.83	70.34	17.83
12.307	7.827	14.189	96.688	29.205	10.13	69.03	20.84
19.355	12.955	14 189	116.043	42 16	8.24	67.31	24.45
13.606	10.46	14.189	129.649	52.62	7.22	65.99	26.79
21.642	16.884	14.189	151.291	69.504	6.04	64.39	29.57
89.28	2.65	37.125	89.280	2 65	28.87	69.08	2.05
22.871	3.714	37.125	112.151	6.364	23 94	71.98	4 08
13.974	3.576	37.125	126.124	9.94	21.52	72.75	5.73
13.072	3 967	37.125	139.196	13.907	19 6	73.10	7.3
47.797	20 627	4.7235	47.797	20 627	6.46	65.34	28 2
3.905	2 911	4 7235	51 702	23.538	5.91	64.65	29 44
2.128	2 114	4.7235	53 830	25.652	5.60	63.93	30.47
5.010	4.487	4.7235	58.840	30.139	5.04	62.80	32.16
5 624	5.529	4.7235	64.464	35.668	4.50	61.48	34.02
9.890	9.596	4.7235	74 354	45.264	3.80	59.79	36.41
11.950	12.619	4.7235	86.304	57.883	3.18	57.95	38 87
11 342	12.563	4 7235	97.646	70.446	2 73	56.50	40.77
10.32	11.895	4.7235	107.966	82.341	2.43	55.36	42.21
38 055	2.56	11.652	38.055	2.56	22.29	72.81	4.90
9.646	5 885	11 652	47.701	5.885	17.86	73.12	9.02
5.745	2.704	11.652	53 446	8.589	15.81	72.53	11.66
4.757	2.510	11 652	58 203	11 099	14.39	71.89	13.72
20.484	11.849	11.652	78.687	22.948	10.29	69.46	20.25
27.379	22 312	0 969	27.379	22 312	1.91	54.05	44.04
1.671	2.631	0.969	29.05	24 943	1.76	52.86	45.38
2.082	3.288	0.969	31.132	28.231	1.60	51.60	46.8
5.945	8.518	0.969	37.077	36.749	1 29	49.57	49.14
5 810	9.005	0.969	42.887	45.754	1.08	47.86	51.06
5.484	8.412	0.969	48.371	54.166	0.94	46.73	52.33
9.274	16.13	0.969	57 645	70 296	0.75	44.72	54.53
6.383	12.541	0.969	64.001	82.81	0.66	43.31	56.03
4.17	8.485	0.969	68.171	91.295	0.6	42.49	56.91
6.92	12.605	0.969	75.091	103.9	0 54	41.73	57.73
3.288	9.302	0.969	78.319	113.202	0.50	40.69	58.81
5.753	14.7	0.969	84.072	127.902	0.46	40.48	60.06

acetone. The method used has already been described. The solubility of calcium chloride in acetone ranging in concentration from 95–100% acetone gave negligible results at 20°. Not very satisfactory results were obtained in determining the solubility of the calcium chloride in aqueous solutions containing 1–10% of acetone. Unless the calcium chloride is added in very small quantities and the solution quickly cooled, considerable heat is generated and the concentration of the acetone solution changes.

The solubility of the anhydrous calcium chloride in 91% water and 9% acetone was found to be 40.5 g. $CaCl_2$ in 100 g. of the solution. This gives one point in the line D Q, Fig. 4. The point D represents the solubility of the salt in water, or 74.5 g. of calcium chloride in 100 g. of water, or 42.70 g. in 100 g. of the solution. The points on the binodal curve were determined in the same manner as those previously described, and are given in Table VI. Acetone was added to a solution which was saturated with calcium chloride at 20°. The acetone dissolved in the solution and no salt was precipitated. With saturated potassium fluoride and carbonate solutions, very little acetone was required to produce two layers, but with the chloride of calcium over 20% of acetone was added before a second layer appeared. The end points in this saturated solution were not easy to obtain, being rather obscure on account of the syrupy nature of the liquid. Time was required to obtain satisfactory conditions of equilibrium and realization of a sharp separation. The points on the other end of the binodal curve are not difficult to obtain. Temperature effects are noticeable with this particular system. From 19 to 20° there is no appreciable clouding, but when the solution is heated from 20 to 21°, immediate cloudiness is noted.

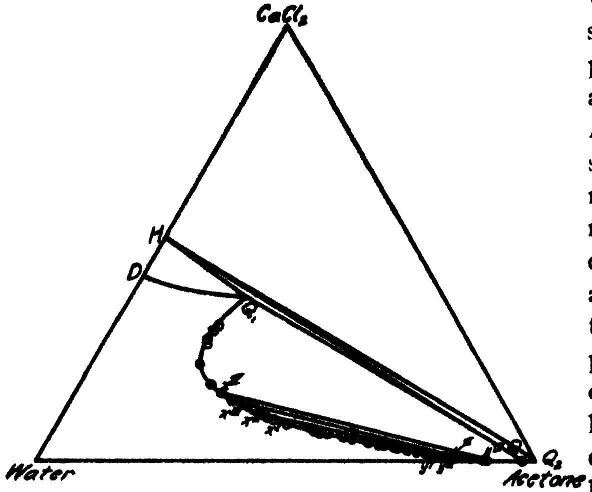

Fig 4.—Equilibrium in the system; calcium chloride, water and acetone.

Determination of Quadruple Points.—Acetone was added to an almost saturated solution of the hexahydrate of calcium chloride in water. The bottle containing the mixture was placed in a thermostat, with a constant temperature of 20°. Every addition of the hydrate increased the amount of water present, making it necessary to add more acetone to produce equilibrium. Finally anhydrous calcium chloride was added and the temperature of the system was allowed to reach 28°. All the calcium chloride went into solution. The flask was again placed in the thermostat, and the contents of the flask were thoroughly agitated and mixed for a day by means of a rotating fan. The contents of the flask were allowed to settle, when the following layers appeared: An upper layer containing acetone and a little water and traces of calcium chloride, then crystals of the hydrate of calcium chloride, a lower layer of a saturated solution of calcium chloride, water and acetone. The lower layer was siphoned off and its acetone and calcium chloride content determined in exactly the same manner as the one previously described. 341.5 g. of the solution, when distilled, gave a mixture of 126.905 g. of acetone and water. The specific gravity found at 20°/4° was 0.8936, at 20°/20° 0.8969. On the tables this corresponds to 61% acetone, or there was 77.41 g. acetone in 126.905 g. of the mixture as well as in the 341.5 g. originally taken. This gives 22.66% of acetone. 33.88 g. of the solution, dehydrated, gave 12.927 g., or 38.16% $CaCl_2$. The crystals were filtered off and dried by suction. They were pressed between several thicknesses of filter paper and rapidly transferred to a weighed bottle. 6.303 g. of the crystals, when heated above 300°, gave a residue weighing 3.18 g. This shows that the crystals were $CaCl_2.6H_2O$.

Analyses of the upper layer gave no weighable amount of calcium chloride. The acetone content was determined in the usual manner, and was found to be 98.4%. A saturated solution of calcium chloride will not remove all the water from acetone. It is wasteful, as it retains over 20% of the acetone.

The second quadruple point was determined by using the 98% acetone, obtained by distillation of the upper solution of the first quadruple point, and adding to it anhydrous calcium chloride; and although an appreciable amount of acetone was present, no liquid seemed to be present, and the contents of the flask appeared as a solid, white crystalline mass. However, when the contents of the flask were stirred with a glass rod, the liquid separated and settled on top. At first it was thought that a compound was formed similar to the compound formed by alcohol and calcium chloride. In 1850, Hlasiwetz[1] stated that powdered calcium chloride formed a compound with pure acetone, which was a dry mass at 100° and only traces of the acetone odor were given off. The formation of this compound is doubtful. After the contents of the flask were stirred repeatedly and kept at 20° for a week the supernatant liquid was decanted off and distilled. Its specific gravity at 20°/4° was 0.7915, which corresponds to 100% acetone. The amount of calcium chloride dissolved in the acetone solution was practically nothing. Anhydrous calcium chloride will completely dehydrate acetone.

Numerous determinations of the tie lines were made in an attempt to locate the plait points accurately, but separation into distinct upper and lower layers were rather difficult to obtain.

The following results were obtained:

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[1] *Jahr. Ber.*, 3, 394; *J. prakt. Chem.*, 51, 355.

TABLE V.

		Amount of solution.	Grams $CaCl_2$.	Grams of $CaCl_2$ in 100 g. of solution.
I.	Lower layer	12.102	2.010	16.61
	Upper layer	9.67	0.018	0.186
II.	Lower layer	23.837	3.090	12.97
	Upper layer	17.018	0.107	0.628
III.	Lower layer	11.586	1.228	10.60
	Upper layer	11.600	0.110	0.948
IV.	Lower layer	17.432	1.961	11.25
	Upper layer	9.355	0.092	0.985
V.	Lower layer	20.949	1.960	9.36
	Upper layer	19.080	0.252	1.321

The calcium chloride content of some of the upper layers was determined by titration with a standard $N/10$ silver nitrate solution. The results did not differ from those obtained by evaporation of weighed quantities of the solution.

Sodium Chloride, Water and Acetone.—The systems previously mentioned contain salts whose dehydrating value depends largely on the vapor tension of their hydrates. When two liquids are miscible in all proportions, the addition of a third component will cause the appearance of two liquid phases, and the third component does not necessarily form a hydrate. This is shown in the case of common salt. As sodium chloride is a very common laboratory agent, its efficiency in salting out acetone was determined. Some work has been done along this line. Linebarger[1] and Snell have shown that two liquids phases will appear when sodium chloride is added to an aqueous solution of acetone. Work of a quantitative nature was done by W. Herz and M. Knoch[2] when they determined the solubility of salt in aqueous solutions of acetone. In their paper they note the solubility of the salt and the formation of layers. The work is of little value as their data are in an unavailable form, for example, the solubility of the salt is expressed in millimols for 100 cc. of the solution which contains the salt, water and acetone. The solubility is plotted on a diagram and the rectangular coördinates are volumes of acetone and millimols of sodium chloride in 100 cc. of the whole solution. No densities nor specific gravities are given. The solubility of sodium chloride in water is given as 537.9 millimols in 100 cc. of the solution, which corresponds to 31.44 g. in 100 cc. of the solution. The only data which corresponds to this are those given by Bödlander,[3] who gives 31.6 g. of sodium chloride in 100 g. of the salt solution, the specific gravity of the solution being 1.203. Herz and Knoch give the limits of the layer formation, which would correspond to the quadruple points, as follows: water

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[1] *Loc. cit.*

[2] *Z. anorg. Chem.*, 41, 319.

[3] *Z. physik. Chem.*, 7, 316.

TABLE VI.

Solvent added at one time.		Total amount of components present.			No. of g. of each component in 100 g. of the solution.		
Water.	Acetone.	CaCl₂.	Water.	Acetone	CaCl₂.	Water.	Acetone.
26.3245	17.289	6.534	26.3245	17 289	13.03	52.49	34.48
8.3095	17.94	6.534	34.634	35 229	8 5	45.37	46.15
5.82	20.183	6 534	40.454	55.412	6.38	39.51	54.11
3.808	16.937	6.534	44.262	72.349	5.35	35.95	58.70
6.28	29.505	6 534	50.542	101.854	4.11	31.8	64.09
3.98	19.596	6.534	54.522	121.45	3.58	29.88	66.54
1.933	13.026	6.534	56.455	134.476	3 31	28.59	68.10
3.824	13 801	6 534	60 279	148.277	3.04	27.03	69 93
2.61	18.098	6.534	62.879	166.375	2.77	26 67	70.56
41.945	25.595	10.904	41.945	25.595	13.90	53.47	32.63
10.707	18.603	10 904	52 652	44.198	10.12	48.86	41.02
6.027	14.933	10.904	58.679	59.131	8.47	45.59	45.94
6.255	22.49	10.904	64.934	81 621	6.92	41.24	51.84
2.72	12.615	10.904	67.654	94.236	6.31	39.15	54.54
6.898	26.902	10.904	74 552	121 138	5.28	36.09	58.63
2.015	11.945	10.904	76.563	133.083	4.94	34.72	60.34
19.553	35.766	2 525	19 553	35 766	4.37	33 8	61.83
10.116	58.96	2 525	29 669	94 726	1.99	23.38	74 63
4.137	26 917	2 525	33 806	121 643	1.6	21.4	77 00
3.362	25.298	2.525	37 168	146 941	1 35	19 92	78 73
45.72	21 423	15 531	45 72	21 423	18 787	55.301	25.913
19.372	22 765	15.531	65 092	44.188	12 443	52.153	35 404
6.932	13 420	15 531	72 024	57.608	10.70	49 61	39 69
5 274	11 441	15 531	77.298	69.049	9.59	47 75	42.66
3.755	10 413	15 531	81.053	79 462	8 82	46 04	45 14
7.709	23 88	15.531	88 762	103 342	7 48	42.75	49 77
2.546	9.612	15 531	91.308	112 954	7 07	41.54	51.39
2.193	8.985	15 531	93 501	121.939	6 72	40 48	52 8
53.372	22.230	32 4593	53 372	22 230	30 04	49 39	20.57
44 551	25.399	32 459	97 922	47 629	18.23	55 01	26.76
15.278	16.33	32 459	113 2007	63.959	15 49	54.00	30.51
16.151	20.506	32.459	129.352	84 465	13 18	52 52	34 3
13.54	24.925	32.459	142.892	109.390	11.40	50 20	38 40
57.272	22.372	31.13	57 272	22 372	28.09	51.71	20 20
3.11	2.216	31.13	60.383	24 588	26.81	52.01	21.18
16.014	5.166	31.13	76.397	29.754	22 67	55 66	21 67
19.84	14 08	31.13	96 237	43 834	18.189	56 21	25 60
41.367	17.903	26.901	41.367	17.903	31.21	48 00	20.81
24.512	71.611	2.197	24.512	71.611	2.23	24.93	72.84
2.310	19.74	2.197	26.822	91 351	1 82	22.27	75.89
18.55	97.606	0.816	18.55	97.66	0.68	15 87	83.44
2.14	19.48	0.816	20.69	117.086	0 58	14.93	84.49
3.389	35.910	0.816	24 079	152.996	0.45	13.55	86.00
8.2145	48.23	0 2735	8.2145	48.23	0 48	14 49	85.13
4.214	40.096	0.2735	12.4285	88.326	0.27	12.31	87.42
1.090	33.45	0.2735	13.5185	121.776	0.20	9.95	89.85
2.92	43.06	0.2735	16.4385	164.836	0.15	9.05	90.81

68, acetone 32 and salt 18.03 in the lower layer, and water 13, acetone 87 and salt 0.45 in the upper layer. This means that in a solution made up of 68 volumes of water and 32 of acetone, salt is dissolved, and 100 cc. of the salt solution so made will contain 18.03 g. of salt. No attempt was made to check these results.

The salt used was Kahlbaum's "Zur Analyse mit Garantieschein." Frankforter and Frary had used the same salt and determined its solubility, so no redetermination of this point was made. The solubility is 35.7 g. in 100 g. of water, or 26.3+ g. in 100 g. of solution. This is given by point D in Fig. 5. The salt used was heated to redness until all decrepitation ceased. It was then cooled in a desiccator and a weighed amount dissolved in as little water as possible at 20°. This gave the saturated salt solution. Acetone was then added to the weighed water and salt solution and the salt was immediately precipitated, the acetone seeming to take the place of the salt. The weight of the acetone added was determined by difference, and more water was added until the salt layer just disappeared. The last traces of salt did not dissolve very readily. This process was continued until the appearance of two layers without salt precipitation. The points on the binodal curve were determined in the same manner as in the other systems, and are given in Table VIII. Toward the end, as the concentration of the acetone increased, the salt was again precipitated on addition of acetone, and water was again added until the salt dissolved. By continuation of this latter process, the solubility of the salt in acetone in concentrations ranging from 86 to 91% of acetone was determined. These determinations are given in Table VII. The solubilities from 91 to 100 are interpolated. The solubility of NaCl at 100 is zero.

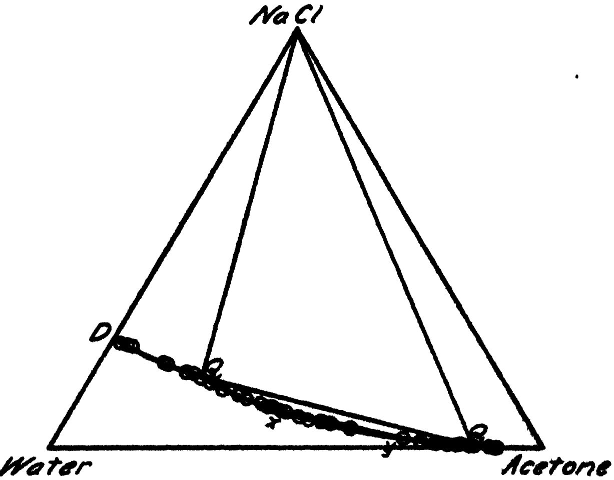

Fig. 5.—Equilibrium in the system: sodium chloride, water and acetone.

In determining the quadruple point, salt was added to an acetone water mixture until there was a large excess of undissolved salt in the bottom of the bottle. The bottle containing the complex was placed in a shaking machine which was operated by an electric motor, and after four days of this thorough shaking the composition of the upper layers was determined in the usual manner. 23.543 g. and 23.65 g. of the upper layer gave 0.110 and 0.103 g. of salt, equal to 0.44 and 0.48 g. of salt in 100 g. of solution, and 22.530 g. of the lower solution gave 3.729 g. of salt or 16.55 g. of salt in the lower solution. The specific gravity determination used before to obtain the amount of acetone in the upper and lower layers was used in this case.

The specific gravity of the solution obtained by complete distillation of the upper layer was 0.8338, which gives an acetone content of 85.8%. Salt dehydrates only to this percentage, showing that it would be of no value in removing water from acetone.

TABLE VII.—SOLUBILITY OF SALT IN ACETONE AND WATER.
Temperature 20°

NaCl.	Water.	Acetone.
25.9	73.06	1.04
24.19	71.18	4.03
25.06	72.00	2.94
20.85	66.78	12.37
20.17	66.01	13.82
18.32	63.16	18.52
20.44	66.19	13.37
17.89	62.21	19.90
0.19	10.82	88.99
0.15	9.62	90.23
0.12	8.94	90.94
0.32	13.92	85.76

TABLE VIII.—BINODAL CURVE OF SALT, WATER AND ACETONE.
Temperature 20°.

Solvent added.		Total amount of components present.			Per cent. components present in 100 g. of soln.		
Water.	Acetone.	Salt.	Water.	Acetone	Salt.	Water.	Acetone
3.921	6.606	12.5163	47.085	19.259	15.87	59.71	24.42
13.511	17.608	12.5163	60.596	36.867	11.38	55.09	33.53
3.567	7.366	12.5163	64.163	44.233	10.35	53.06	36.59
3.166	8.134	12.5163	67.329	52.367	9.47	50.92	39.61
2.424	6.567	12.5163	69.753	58.934	8.87	49.39	41.74
3.025	6.336	12.5163	72.778	65.270	8.31	48.33	43.36
3.905	11.80	12.5163	76.683	77.07	7.53	46.12	46.35
3.162	12.25	12.5163	79.845	89.32	6.89	43.95	49.16
1.884	10.454	12.5163	81.729	99.774	6.45	42.12	51.43
3.882	15.40	12.5163	85.611	114.984	5.87	40.19	53.94
8.94	34.928	1.3838	94.551	149.912	4.87	36.79	58.34
16.3322	42.188	1.3838	16.3222	42.188	2.31	27.27	70.42
4.79	23.723	1.3838	21.1222	65.901	1.57	23.89	74.54
2.893	16.897	1.3838	24.0152	82.808	1.27	22.19	76.54
3.99	36.566	1.3838	28.0052	119.374	0.93	18.83	80.24
3.144	25.340	1.3838	31.1492	144.714	0.79	17.58	81.63
7.392	40.153	0.2840	7.392	40.153	0.59	15.46	83.95
4.97	76.208	0.2840	12.362	76.208	0.32	13.92	85.76

259.79 g. of the lower solution, which was distilled until the temperature remained at 100° over five minutes, gave 83.645 g. of a distillate which had a specific gravity of 0.8810. This corresponds, on the McElroy and Krug tables, to 67.9% acetone; or, in 83.645 g. there are 56.80 g. of acetone, which is equivalent to 21.86%. Then the upper layer contained 85.8% acetone and 0.45% of sodium chloride, while the lower layer contained 21.86% acetone and 16.55% salt. These points check with the points which were obtained in the determination of the binodal curve. The points on the binodal curve are given in Table VIII. Tie lines were determined in an effort to locate the plait point. The solubilities of salt in the different concentrations of acetone, the binodal curve, the quadruple point and the tie lines are all indicated in Fig. 5.

In determining points on the line D Q, some were obtained by the method used for determination of the binodal curve, but a few were directly determined. To a solution containing 98.6 parts water and 1.4 acetone by weight, salt was added and the flasks were well shaken. The temperature was kept at 20°. It was found that 15.9 g. salt were present in 100 g. of the salt solution. In a similar manner the solubilities of salt in a 96.10 and a 93.9% water acetone solution were determined. 24.19 g. of salt were present in 100 g. of a 93.9% water acetone solution and 25.06 g. of salt were present in a 96.10% solution. These points are given in Table VII, which gives the solubility of salts without appearance of layers.

Temperature Effects.—Acetone and water are two liquids miscible in all proportions. Lowering or raising the temperature will not cause the formation of two layers unless a third substance, such as calcium chloride, potassium fluoride or sodium chloride is added. In the discussion of the binodal curve in the calcium chloride system, attention was called to the fact that when a homogeneous mixture of calcium chloride, water and acetone at 20° (the temperature chosen for this isotherm) was slightly warmed, two liquid phases formed immediately. With solutions containing a high sodium chloride or potassium fluoride content, the same phenomenon was noticed. In more dilute solutions the effect was not apparent. Tables IX, X and XI give the results obtained when just homogeneous solutions of these salts and aqueous acetone were warmed from temperatures ranging from 5 to 40°. Temperatures above 40° were not used because acetone is very volatile, and in working at temperatures above 30° there was a loss in acetone. Pressure flasks were not used. It was thought that an increase in the pressure might have some effect on the results. The pressure used in all the experiments was that of the atmosphere.

The method used has been described. A definite amount of salt was weighed in the Erlenmeyer flask that contained the thermometer and the same process was used as in the determination of the binodal curve. The temperature of the first determination was kept as near 5° as possible, and water was then added until the two layers just disappeared. The addi-

Table IX.—Binodal Curve Points at Varying Tempertaures in the System Potassium Fluoride, Water and Acetone

Temperature.	Potassium fluoride.	Water.	Acetone.	Total.	Water added.	Per cent. potassium fluoride.	Per cent. water.	Per cent. acetone.
10°	6.548	41.773	11.426	59.747	41.773	10.96	69.91	19.13
15°	6.548	42.153	11.426	60.127	0.380	10.89	70.10	19.01
20°	6.548	42.663	11.426	60.637	0.510	10.80	70.36	18.84
25°	6.548	43.283	11.426	61.257	0.620	10.68	70.65	18.67
30°	6.548	44.72	11.426	62.694	1.437	10.44	71.34	18.22
35°	6.548	44.87	11.426	62.844	0.150	10.41	71.44	18.18
10°	8.045	69.784	32.481	110.310	69.784	7.29	63.27	29.44
15°	8.045	69.784	32.481	110.310	0.000	7.29	63.27	29.44
20°	8.045	70.069	32.481	110.595	0.285	7.27	63.36	29.37
25°	8.045	71.274	32.481	111.800	1.205	7.19	63.76	29.05
30°	8.045	72.824	32.481	113.350	1.550	7.10	64.24	28.66
35°	8.045	73.884	32.481	114.410	1.06	7.04	64.57	28.39
8°	15.915	81.620	15.41	112.945	81.620	14.09	72.27	13.64
15°	15.915	83.00	15.41	114.325	1.38	13.92	72.60	13.48
20°	15.915	84.69	15.41	116.015	1.69	13.73	72.99	13.28
25°	15.915	86.06	15.41	117.385	1.37	13.56	73.31	13.13
30°	15.915	87.54	15.41	118.865	1.48	13.39	73.65	12.96
35°	15.915	88.58	15.41	119.905	1.04	13.28	73.87	12.85
0°	15.915	90.04	24.34	130.295	90.04	12.22	69.11	18.67
10°	15.915	92.02	24.34	132.275	1.980	12.04	69.56	18.40
15°	15.915	93.84	24.34	134.095	1.82	11.87	69.98	18.15
20°	15.915	96.24	24.34	136.495	2.40	11.65	70.51	17.84
25°	15.915	98.04	24.34	138.295	1.80	11.51	70.89	17.60

Table X.—Temperature Effect in the System Sodium Chloride, Water and Acetone.

Temperature.	Sodium chloride.	Water.	Acetone	Total.	Water added	Per cent. sodium chloride.	Per cent. water.	Per cent. acetone.
13°	14.44	51.96	25.88	92.28	51.96	15.64	56.30	28.06
15°	14.44	52.875	25.88	93.195	0.195	15.50	56.74	27.76
20°[1]	14.44	55.760	25.88	96.080	2.885	15.03	58.04	26.93
25°	14.44	56.50	25.88	96.82	0.74	14.91	58.36	26.73
30°	14.44	57.66	25.88	97.98	1.16	14.74	58.85	26.41
35°	14.44	58.74	25.88	99.06	1.08	14.58	59.30	26.12
40°	14.44	60.45	25.88	100.77	1.71	14.33	59.98	25.69
10°	14.44	61.15	43.38	118.97	61.15	12.14	51.40	36.45
15°	14.44	62.25	43.38	120.07	1.10	12.03	51.84	36.13
20°	14.44	64.45	43.38	122.27	2.20	11.81	52.71	35.48
25°	14.44	66.15	43.38	123.97	1.70	11.65	53.36	34.99

[1] Note.—The reading at 20° is too high and at 25° too low, too much water was added at 20°. 3.62 g. of water were added to give homogeneity in the solution in raising the temperature of the solution from 15° to 25°. The temperature effect is most noticeable around 20°.

tional water was weighed. The contents of the flask were allowed to warm to 10°, cloudiness appeared, water was added until the cloudiness just disappeared, and the increase in water was determined by weighing. The solution was then warmed to the different temperatures, water being added until homogeneity was obtained at the temperatures given. Variations are noted in the tables.

TABLE XI.—TEMPERATURE EFFECTS IN THE SYSTEM CALCIUM CHLORIDE, WATER AND ACETONE.

Temperature.	Calcium chloride.	Water.	Acetone.	Total.	Water added.	Per cent. calcium chloride.	Per cent. water.	Per cent. acetone.
10°	15.430	34.969	14.86	65.255	34.965	23.64	53.59	22.77
20°	15.430	36.505	14.86	66.795	1.540	23.10	54.65	22.25
25°	15.430	39.045	14.86	69.335	2.540	22.25	56.31	21.44
30°	15.430	40.505	14.86	70.795	1.460	21.79	57.22	20.99
35°	15.430	43.485	14.86	73.775	2.980	20.91	58.95	20.14
40°	15.430	44.675	14.86	74.965	1.190	20.58	59.59	19.83
5°	15.430	53.065	30.89	99.385	53.065	15.52	53.39	31.09
15°	15.430	53.065	30.89	99.385	0.000	15.52	53.39	31.09
20°[1]	15.430	54.695	30.89	101.015	1.630	15.27	54.15	30.58
25°	15.430	57.245	30.89	103.565	2.550	14.89	55.28	29.83
30°	15.430	59.225	30.89	105.545	1.98	14.62	56.11	29.27
35°	15.430	61.715	30.89	108.035	2.49	14.29	57.12	28.59
40°	15.430	64.395	30.89	110.715	2.68	13.93	58.17	27.90

The preceding method was used in trying to determine the critical solution temperature of the various solutions of the salts in water and acetone mixtures. The temperature at which any two conjugate solutions become homogeneous is called the critical solution temperature. A complete discussion of the critical solution temperature is given by Timmermans.[2]

W. Dolgolenko[3] states that the lower critical solution temperature of two solutions is due to the presence of an impurity, as a lower critical solution temperature is characteristic of ternary mixtures. V. Rotmund[4] states that the clouding is not dependent upon the third substance but is an optical property. Exception must be taken to this statement, as it seems very evident in the foregoing experiments that the clouding is dependent on the amount of the third substance present.

J. Snell,[5] in working with salts and mixtures of acetone and water, found that all of the solutions with which he worked (with the exception of those which contained the salts, sodium sulfate, sodium carbonate, disodium phosphate and sodium ammonium phosphate) clouded when they were warmed. Linebarger[5] stated that the lower the temperature the more water is needed to bring about the disappearance of the layers. A fall of a few degrees will bring characteristic cloudiness in a solution of potassium carbonate in a mixture of alcohol and water. Traube and Neuberg[1] show that temperature will affect the composition of the two layers when the two solutions are heated, the lower layer increasing in volume and the upper layer decreasing. Saturated solutions of calcium chloride, sodium chloride, and potassium fluoride, were made and acetone added until the concentration of the solutions was that obtained at the quadruple point. Upon increasing the temperature all the lower layers clouded, showing that the room temperature was the lower critical temperature of these solutions. When the upper solutions were heated, neither the calcium chloride nor the potassium fluoride was affected. This would be expected, as practically no salt is in the solution in either of these two upper layers. The upper layer of the sodium chloride solution clouded when it was warmed. This was not expected, as it would indicate that the plait point was not independent of the temperature and all the isotherms would not cross at this point.

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[1] NOTE.—The change occurred at 18°.

[2] *Z. physik. Chem.*, **58**, 129–213; *Z. Electrochem.*, **12**, 644.

[3] *Z. physik. Chem.*, **62**, 499.

[4] *Ibid.*, **63**, 54.

[5] *Loc. cit.*

The concentrations of all the solutions were changed and the effect of warming and cooling the different layers was noted. On cooling no effect was noticed, but when any of the solutions were warmed they clouded, and when cooled to the original temperature they cleared. A more thorough investigation of this phenomenon is to be made.

Determination of Acetone.—If salts are added to homogeneous mixtures of some organic liquids and water, the solutions become turbid, sometimes at room temperature and sometimes at higher or lower temperatures. Frankforter and Frary used this principle in determining the amount of ethyl alcohol in an aqueous solution. Quantitative results were obtained. They added to a liquid of unknown alcoholic contents enough of the salt to cause the solution to separate into two layers and then, by cautious addition of water, made the solutions just homogeneous. The salt giving the most satisfactory results was potassium fluoride. Snell uses a similar plan with solutions containing acetone in water. The salt used in his case was potassium chloride. Instead of adding more salt or water to obtain homogeneity he increases or decreases the temperature until the solution just gives two layers. The temperatures and the aqueous acetone solutions are plotted as coördinates, and a curve is drawn through the points obtained experimentally. This method can be used only with mixtures containing 20–85% of acetone and would not be accurate for mixtures containing 50 or 60% acetone because of the flatness of the curve. The results are not satisfactory if a third substance is present. The temperatures range from 32 to 46°. Potassium chloride is not a very satisfactory agent for the salting out of acetone. The value of potassium fluoride in this respect has already been shown.

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[1] *Z. physik. Chem.*, 1, 510.

New Method for Determination of Acetone.—In the determination of the binodal curve, there is only one concentration for any given quantity of potassium fluoride in 100 g. of the just homogeneous mixture. Since the acetone, water and salt solution conducts itself in the same manner as the alcohol, water and salt solution, the percentage of acetone in any aqueous solution can be determined in exactly the same manner as Frankforter and Frary determined alcohol. In Table I it will be necessary to recalculate all values given so that the sum of the acetone and water will always be represented by 100 g. of the solvent. The amounts of potassium fluoride will be changed. By plotting the aqueous acetone solution and the potassium fluoride as rectangular coördinates, a curve is obtained. When a solution contains an unknown quantity of acetone, a definite amount of the liquid is weighed out, and the salt is added until two liquid phases just appear, then additional water is added until the two layers just disappear, and the additional water is weighed. The total volume of the solvent and the amount of the potassium fluoride used are known. These are calculated in the form, x g. of potassium fluoride to 100 g. of solvent. There is only one point on the curve which corresponds to x grams of potassium fluoride. From this point the other coördinate or the percentage of aqueous acetone can be directly determined. When this is higher than 60, it is advisable to dilute the solution, as this method gives more accurate results for solutions containing between 1 and 60% of acetone. While the carbonate of potassium and the chloride of sodium and calcium could be used, they would not be as satisfactory. The end points with potassium carbonate are not sharp. Calcium and sodium chloride do not give results with solutions containing less than 21% of the acetone.

While this is a neat and rapid method for the determination of acetone in pure aqueous solutions, its value would be far greater if it could be used in the presence of a third substance, such as methyl or ethyl alcohol or the higher ketones. None of the higher ketones were available, so the efficiency of the method in the presence of these could not be tried. The method is not efficient in the presence of ethyl alcohol, because ethyl alcohol is salted out by potassium fluoride. With methyl alcohol, absolutely satisfactory results were not obtained. When a solution of methyl alcohol containing small quantities of acetone was tested by this method, no results were obtained. So the presence of small amounts of acetone in methyl alcohol cannot be determined quantitatively. More satisfactory results were obtained in testing the effects of small quantities of methyl alcohol in the presence of large quantities of acetone, as indicated in Tables XII and XIII.

A definite mixture of methyl alcohol and acetone was made up by weight. The method for the determination of the binodal curve was used, only the mixture of acetone and methyl alcohol was used in place of the pure acetone. Fairly good results are obtained in this determination. Acetone can be determined in the presence of methyl alcohol, provided the acetone is in excess and not the methyl alcohol.

TABLE XII.—POTASSIUM FLUORIDE, METHYL ALCOHOL, ACETONE AND WATER.
Temperature 20°.

KF.	Water.	Mixture. Alcohol acetone	Alcohol.	Acetone.	Per cent. KF.	Per cent. water	Per cent. alcohol.	Per cent. acetone.	Per cent. mixture, water and alcohol.
16.949	34.46	0.636	0.0727	0.5633	32.58	66.20	0.14	1.08	66.34
16.949	62.030	0.4977	0.5691	4.408	20.19	73.88	0.68	5.25	74.56
16.949	83.571	14.825	1.694	13.130	14.69	72.45	1.46	11.40	73.91
16.949	102.809	28.486	3.256	25.230	11.43	69.35	2.19	17.02	71.54
16.949	117.712	43.455	4.966	38.489	9.52	66.09	2.79	21.60	68.88
16.949	137.936	68.43	7.82	60.609	7.59	61.77	3.50	27.14	65.27
19.2975	86.797	13.514	. .		16.13	72.57	1.40	9.90	73.97
19.2975	119.047	34.075	....	. .	11.19	69.05	2.45	17.31	71.50
19.2975	141.237	63.423	...	.	8.62	63.07	3.51	24.80	66.58
19.2975	155.695	83.221	.	. . .	7.47	60.30	4.00	28.73	64.30

By referring to Fig. 1, the weights of water and acetone corresponding to the above quantities of potassium fluoride are found, and are the following:

TABLE XIII.

KF.	Acetone	Water.	(Last column, Table XII.)
32.58	1.42	66.0	66.34
20.19	5.81	74.00	74.56
14.69	11.81	73.5	73.91
11.43	17.57	71.0	71.54
9.52	22.48	68.0	68.88
7.59	28.41	64.0	65.27
16.13	9.87	74.0	73.97
11.19	17.81	71.0	71.5
8.62	25.38	66.0	66.58
7.47	28.53	64.0	64.30

If the weights in the last column of Table XII are compared with the weights given in the third column of Table XIII, it will be seen that the methyl alcohol does not interfere to any marked extent in the determination of acetone by this method. This holds true if the amount of methyl alcohol is not too high. In the first six determinations a solution containing 92.87 g. of acetone and 11.99 g. of methyl alcohol was used, and in the last four determinations 139.895 g. of acetone and 19.775 g. of methyl alcohol.

Summary.

In the study of the four systems, it has been shown that potassium fluoride and potassium carbonate in the anhydrous form are equally efficient in dehydrating acetone. Potassium fluoride is the more rapid agent of the two, and gives cleaner cut separations. If a large excess of anhydrous calcium chloride is used, the acetone is completely dehydrated. Sodium chloride dehydrates to 85.8% of acetone.

The saturated solution of potassium fluoride will dehydrate to 98%, while the saturated potassium carbonate dehydrates only to 96.5% of acetone. 98.4% acetone can be obtained with a saturated calcium chloride solution.

Neither the fluoride nor the carbonate solutions entail much loss of acetone, practically no acetone being soluble in these saturated solutions, while calcium chloride retains 23% of acetone in the aqueous solution of the chloride. Sodium chloride is the least satisfactory of the four, as it retains over 21% of acetone, and in addition dehydrates only to 85.8%. The viscid nature of the calcium chloride solution is objectionable. The fluoride gives the cleanest and most rapid separation and seems to be the most satisfactory salting out or dehydrating agent for acetone.

This investigation covers the following lines:

1. The isotherms at 20° for the systems water, acetone, and potassium fluoride, water, acetone and potassium carbonate, water, acetone and calcium chloride and water, acetone and sodium chloride are given and thoroughly investigated.
2. Temperature effects in the systems are noted, and while no upper critical solution temperatures were found, the lower critical solution temperatures of a series of solutions are given.
3. A quantitative method is given for the determination of acetone in an aqueous solution, provided a third substance is not present. The effect of the presence of methyl alcohol, when this method is used, is discussed.

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A NEW METHOD FOR THE DETERMINATION OF THORIUM IN MONAZITE SAND.

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The large amount of work published upon the determination of thorium in monazite sand is an indication of the importance of this problem. Several methods have been devised for this determination. The principal ones, up to the year 1910, were the ammonium oxalate method,[1] the thiosulfate method,[1] the hydrogen peroxide method,[2] the fumaric acid method,[3] and the nitrobenzoic acid method;[4] the thiosulfate method being the one usually employed.

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[1] Glaser, *Chem. Ztg.*, 20, 612 (1896).

In all of these, as well as in the more recent volumetric molybdate method,[5] it is necessary to precipitate the thorium, and other rare earth elements, as oxalates from the solution of the sand, in order to separate them from the phosphoric acid. This precipitation and the subsequent treatment of the oxalate precipitate, in order to dissolve it and obtain a neutral solution of the rare earth salts, requires considerable time. Potassium trinitride[6] and sebacic acid[7] have also been proposed as reagents for the separation of thorium from the other rare earth elements. A neutral or only slightly acid solution is required, so these methods could not be applied to the analysis of monazite sand without first precipitating with oxalic acid.

The only methods in which the thorium is precipitated from the solution of the sand, in the form of a salt other than the oxalate, are the iodate method[8] of Meyer and Speter and the hypophosphate method[9] of Rosenheim. These are both known as "rapid methods."[10]

The iodate method gives very accurate results. Meyer and Speter have tested the method thoroughly on pure solutions and on a sand which had been analyzed in the laboratory of Dr. Gilbert, of Hamburg, in which laboratory the determinations for the German thorium industry are made.[11] The results compared very well with the result obtained by Dr. Gilbert. Although the reagent used is expensive, this expense is outweighed by the gain in working time. The method requires considerable care to avoid loss in the numerous transfers of the precipitate of thorium iodate from the paper to a beaker.

One cannot judge as to the accuracy of the hypophosphate method, as Rosenheim gives no results, either upon pure solutions or upon sands. The reagent, sodium hypophosphate, cannot now be purchased.

Several years ago we noticed that the pyrophosphates of thorium, ceric cerium, and zirconium are insoluble in dilute acids, while the pyrophosphates of cerous cerium and the other rare earth elements are readily soluble in dilute acids. This difference in the solubility of the pyrophosphates is the basis of the new method for the determination of thorium presented in this paper.

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[1] Hintz u. Weber, *Z. anal Chem.*, 36, 27 (1897); Drossbach, *Z angew. Chem.*, 14, 655 (1901); Hauser u. Wirth, *Ibid.*, 22, 484 (1909).

[2] Wyrouboff and Verneuil, *Compt. rend.*, 126, 340 (1898); *Bull. soc. chim.*, [3] 19, 219 (1898); Benz, *Z. angew. Chem.*, 15, 297 (1902).

[3] Metzger, THIS JOURNAL, 24, 901 (1902).

[4] Neish, *Ibid.*, 26, 780 (1904).

[5] Metzger and Zons, *J. Ind. Eng. Chem.*, 4, 493 (1912).

[6] Dennis and Kortright, *Am. Chem. J.*, 16, 79 (1894); Dennis, THIS JOURNAL, 18, 947 (1896).

[7] Smith and James, THIS JOURNAL, 34, 281 (1912).

[8] *Chem. Ztg.*, 34, 306 (1910).

[9] *Ibid.*, 36, 821 (1912).

[10] Meyer und Hauser, "Die Analyse der seltenen Erden und der Erdsäuren," page 263.

[11] Meyer u. Speter, *Chem. Ztg.*, 34, 306 (1910).

Thorium pyrophosphate has been mentioned very little in the literature. Cleve,[1] in 1874, in a paper on thorium salts, made note of the fact that pyrophosphoric acid, when added to a thorium salt, precipitates $ThP_2O_7.2H_2O$, and that this salt dissolves in an excess of sodium pyrophosphate, forming $Na_4Th(P_2O_7)_2.2H_2O$. The various chemical handbooks and dictionaries give these formulas and refer to the article by Cleve. The striking difference in the solubility of the pyrophosphates in acids has apparently not been noticed.

The normal sodium salt, $Na_4P_2O_7.10H_2O$, is the most convenient pyrophosphate to use for precipitating the thorium. It is inexpensive and is readily obtained. A water solution of this salt is very stable, and there is no appreciable hydrolysis to orthophosphate even after standing for a long time or on heating.

Thorium pyrophosphate dissolves readily on heating with an excess of sodium pyrophosphate. It dissolves with difficulty in a large excess of pyrophosphoric acid and is precipitated from this solution slowly by heating, and rapidly by adding a strong acid and heating. It is soluble also in ammonium carbonate and in alkali oxalate solutions. From solutions of the double pyrophosphate, thorium is completely precipitated by boiling with an excess of sodium hydroxide. It is not precipitated from this solution by ammonium hydroxide or by oxalic acid; if the solution is strongly acidified after adding oxalic acid, a mixture of oxalate and pyrophosphate is precipitated. The addition of a strong acid to the double pyrophosphate breaks it up and causes the precipitation of thorium pyrophosphate.

In order to precipitate thorium completely as the pyrophosphate, the solution must be boiled after adding the sodium pyrophosphate, otherwise 1–2 mg. of thorium will remain in solution. The acidity should be about 0.3 *N* or equal to 5 cc. of hydrochloric acid (1.19) in 200 cc. of solution. If the acidity is very much too low, some thorium may fail to be precipitated by going into the form of the double pyrophosphate; if too high, the solvent effect of the acid comes into play. The acidity may, however, vary within fairly wide limits without the loss of any thorium. Zirconium is completely precipitated from a solution under the same conditions as thorium.

The pyrophosphates of cerous cerium, praseodymium, neodymium, lanthanum, yttrium, ytterbium, and erbium are soluble in an excess of sodium pyrophosphate. Freshly precipitated pyrophosphates of each of these metals, equivalent to about 125 mg. of the oxide, when suspended in 100 cc. of water, dissolved readily on the addition of 1–1.5 cc. of dilute hydrochloric acid (1.10). On adding bromine water to the solution of cerous pyrophosphate in dilute hydrochloric acid and heating, a white precipitate of ceric pyrophosphate formed immediately.

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[1] *Bull. soc. chim.*, [2] 21, 116.

Thorium pyrophosphate may be ignited by drying the precipitate, removing it from the paper, burning the paper at as low a temperature as possible, then adding the main body of the precipitate and igniting for about fifteen minutes. Long-continued ignition causes a slight loss of P_2O_5. As is the case in the ignition of other phosphates, it is difficult to burn off all of the carbon. Thorium oxalate is readily changed to the oxide by ignition. Since it is necessary to precipitate as the oxalate at some point in the analysis of monazite sand, in order to remove zirconium (zirconium oxalate being soluble in an excess of oxalic acid) it seemed advisable to precipitate the thorium finally as the oxalate and ignite and weigh the oxide.

It was quite difficult to find a really satisfactory method for changing the pyrophosphate quantitatively to oxalate. The first method tried was to change the pyrophosphate to hydroxide by boiling with sodium hydroxide. Other thorium precipitates, for example the thiosulfate and oxalate, are readily changed to hydroxide in this way. This method was not successful, the transposition not being at all complete. The next method tried was to dissolve the pyrophosphate in an excess of warm sodium pyrophosphate, change the thorium to hydroxide by boiling with sodium hydroxide, filter and wash this precipitate, dissolve it in hydrochloric acid and precipitate the thorium as oxalate. This was not entirely satisfactory, on account of the difficulty in washing out all of the soluble pyrophosphate from the thorium hydroxide. Similar methods applied to the solutions in ammonium carbonate and oxalate were unsatisfactory.

We next tried dissolving the thorium pyrophosphate in concentrated sulfuric acid and oxidizing the filter paper. Instead of the use of sodium nitrate for this purpose, as is customary, we made use of ammonium perchlorate.[1] By the use of concentrated sulfuric acid and a small amount of ammonium perchlorate, a 15 cm. filter paper, containing about 200 mg. of moist thorium pyrophosphate, will be completely destroyed, the pyrophosphoric acid changed to orthoacid, and the thorium brought into solution in about ten minutes. The dry paper, alone, can be destroyed in much less time. Using sodium nitrate, as in the hypophosphate method, one or two hours would have been required. The amount of ammonium perchlorate used is small and the reagent is inexpensive. On cooling and adding water to the mixture of concentrated sulfuric acid and thorium sulfate, a clear solution results. To change the thorium completely to an oxalate entirely free from phosphate, it was found best to first change the sulfate to hydroxide by boiling with sodium hydroxide, filter this, dissolve it in hydrochloric acid and precipitate as oxalate. This was found to give much more satisfactory results than neutralizing with ammonium hydroxide, adding acid until the precipitate dissolves and precipitating with oxalic acid, the procedure in the hypophosphate method.

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[1] We are indebted to H. H. Willard for this suggestion. Potassium perchlorate may also be used, but in this case the sulfates dissolve more slowly, probably due to the formation of a double sulfate. The excess of the potassium salt remains largely undissolved.

This method was first tested on pure solutions of rare earth salts. Pure thorium nitrate was prepared from the commercial salt by the method of Wyrouboff and Verneuil,[1] consisting of a double precipitation of the thorium by hydrogen peroxide. After dissolving the pure salt in water, the strength of the solution was determined by precipitating the thorium from a measured volume in a dilute acid solution as the oxalate, allowing this to stand over night, then filtering and igniting to the oxide. The cerium, praseodymium, neodymium, and lanthanum salts were the double ammonium nitrates. The sodium pyrophosphate solution was made up by dissolving 25 g. of $Na_4P_2O_7.10H_2O$ in 500 cc. of water. The ammonium perchlorate was the commercial salt purchased from Kahlbaum. As this left a slight residue on dissolving in water, it was purified by one recrystallization.

The completeness of the precipitation of thorium by sodium pyrophosphate is shown by the following experiments:

To 35 cc. of pure thorium nitrate solution, 5 cc. of HCl (1.19) were added and the solution diluted to 200 cc. It was then heated to boiling and 10 cc. of the sodium pyrophosphate solution were dropped in slowly from a pipet with constant stirring. The solution was then gently boiled for five minutes, stirring occasionally to keep the precipitate in suspension. The precipitate was allowed to settle for five or ten minutes and was then filtered[2] and washed with water containing a small amount of hydrochloric acid (one or two drops of acid in 200 cc.). The paper containing the moist precipitate was put into a 125 cc. Soxhlet[3] flask and 15 cc. of sulfuric acid (1.84) and a few crystals of ammonium perchlorate were added. The flask was then covered with a watch glass which was held slightly away from the top of the flask by three small bent glass rods in order to allow escape of gases. The flask was heated gently and the heating continued until a brown solution was obtained. The flame was then removed for a moment and more ammonium perchlorate carefully added. Heating was then resumed. More perchlorate was added if necessary. In a short time the solution became colorless and the carbonaceous matter had been entirely oxidized. The solution was then allowed to cool. The flask was placed in cold water and about 75 cc. of distilled water were slowly added with stirring. In a short time a clear solution resulted. This solution was then poured slowly into a solution of 30 g. of sodium hydroxide in about 125 cc. of water, and the flask was washed out with distilled water, collecting the washings in the sodium hydroxide solution. The solution was stirred and boiled for several minutes to convert the thorium to hydroxide. The hydroxide was filtered on a hardened filter paper, using slight suction. This was washed thoroughly with hot water. The paper containing the thorium hydroxide was then placed in the beaker in which the hydroxide precipitation had been made, and 5 cc. of hydrochloric acid (1.19) were added. This was allowed to remain in contact with the paper for a short time and then the solution was diluted and boiled. The paper was filtered off and washed thoroughly. A solution of 2 g. of oxalic acid was added to the filtrate and this was diluted to about 450 cc. and allowed to stand warm over night. The oxalate was filtered, washed with water containing a trace of hydrochloric acid, and ignited to oxide. The amount of thorium oxide taken was 0 1376 g. The amounts found in three experiments were: (1) 0.1384 g., (2) 0.1374 g., (3) 0 1376 g. The filtrate from the thorium pyrophosphate gave no precipitate on boiling with sodium hydroxide or ammonium hydroxide, or on adding oxalic acid and allowing to stand.

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[1] *Loc. cit.*

[2] Thorium pyrophosphate offers no difficulty in filtration, the much more bulky orthophosphate, however, is very hard to filter.

[3] A Kjeldahl flask was later found to be preferable, as it eliminates all chance of loss by spattering.

Experiments were then carried out to determine if a quantitative separation of thorium from the other rare earth elements can be obtained by one precipitation with sodium pyrophosphate. The acidity and volume of solution were the same as in the previous experiments:

Experiment 1.—Weight of ThO_2 taken: 0.1376 g.; weight of CeO_2 taken: 0.1235 g.; weight of ThO_2 found: 0.1413 g. Weight of CeO_2 carried down with the thorium was 3.7 mg.

Experiment 2.—Weight of ThO_2 taken· 0 1376 g.; weight of Pr_4O_7 taken: 0.1241 g.; weight of ThO_2 found: 0.1409 g. Weight of Pr_4O_7 carried down with the thorium was 3.3 mg.

Experiment 3.—Weight of ThO_2 taken: 0.1376 g.; weight of Nd_2O_3 taken: 0.1240 g.; weight of ThO_2 found: 0.1392 g. Weight of Nd_2O_3 carried down with the thorium was 1.6 mg.

The oxides in Experiments 2 and 3 were quite strongly colored.

It was seen that a second precipitation of the thorium as pyrophosphate would be necessary in order to remove the small amounts of rare earth salts that are carried down. This reprecipitation was easily accomplished. The sulfate solution of the pyrophosphate precipitate was rinsed into a beaker and ammonium hydroxide added until alkaline. A few drops of methyl orange were added and hydrochloric acid dropped in until a neutral reaction was obtained, then 7.5 cc. of hydrochloric acid (1.19) were added and the solution diluted to 300 cc. The solution was heated to boiling and precipitated with sodium pyrophosphate as before. The pyrophosphate was filtered, washed, and converted to sulfate, hydroxide and oxalate in the manner previously described.

In a number of experiments this method was tried upon thorium salts alone, and a complete recovery of the thorium was made in each case. When tried upon mixtures of thorium and other rare earth salts, the thorium oxide obtained was in all cases entirely pure. The results obtained are shown in Table I.

TABLE I.

ThO_2 taken. Gram.	CeO_2 taken. Gram.	La_2O_3 taken. Gram.	Pr_4O_7 taken. Gram.	Nd_2O_3 taken. Gram.	ThO_2 found. Gram.
0.1376	....	....	....	....	0.1375
0.1376	....	....	....	....	0.1372
0.1376	....	....	....	....	0.1371
0.1376	0.1235	....	....	....	0.1377
0.1376	0.2470	....	....	....	0.1371
0.1376	....	0.1250	....	....	0.1374
0.1376	....	....	0.1241	....	0.1376
0.1376	..	....	0.1241	....	0.1371
0.1376	...	.. .	....	0.1240	0.1366
0.1376	....	....	....	0.1240	0.1375
0.1376	....	0.1250	0.1241	0.1240	0.1383
0.1376	0.1235	0.1250	0.1241	0.1240	0.1374

This method was then tested upon monazite sand. The best method for the decomposition of the sand seemed to be the one used by Meyer and Speter, taking a 50 g. sample of the unground sand and decomposing it with 100 cc. of concentrated sulfuric acid. The sulfates may then be dissolved in water, filtered, diluted to one liter, and aliquot portions taken for analysis. A 50 cc. portion should be diluted to about 440 cc., in order to obtain the acidity used in the experiments on pure solutions. On precipitating the thorium from this solution with sodium pyrophosphate, a small deposit of ceric pyrophosphate formed on the bottom of the beaker, and this was very difficult to remove. By diluting the solution to 450 cc. and adding 5 cc. of concentrated hydrochloric acid, this did not occur. In carrying out the method in the same manner as on pure solutions, many good results were obtained, but in some cases the results were slightly too high and the final oxide had a faint pink or brown color. This was caused by a trace of rare earth phosphate not dissolving in the hydrochloric acid and thus being carried along with the thorium. This was avoided by precipitating the sulfate solution with sodium hydroxide instead of ammonium hydroxide, filtering and washing the precipitate and dissolving it in the proper amount of acid. This process, of course, involves the use of an additional hydroxide filtration, but as the hydroxide is filtered with suction and the filtration and washing are rapid, but little more time is required than in the other method. An experiment on pure thorium nitrate solution showed that no thorium is lost by this variation in the method; weight of ThO_2 taken was 0.1376 g., weight recovered was 0.1379 g.

In the presence of a large amount of cerium, such as is found in monazite sand, it was found advisable to add a little sulfurous acid solution to reduce any ceric cerium before precipitating the second time as the pyrophosphate.

The complete method as applied to monazite sand is as follows: 50 g.

of the sand are heated to about 250° with 100 cc. of concentrated sulfuric acid in a thick-walled iron dish until complete decomposition is obtained.[1] This will require from 5–8 hours. The dish is kept covered with a watch glass during the heating. The excess of sulfuric acid is not driven off. The mixture is cooled and introduced slowly into about 400 cc. of cold water contained in a large beaker. This beaker is kept surrounded with cold water. The mixture is stirred with a wide spatula and allowed to stand until the sulfates are dissolved. The solution is then filtered through a folded filter paper into a one liter flask, the paper washed, and the filtrate diluted to the mark. Of this solution, 50 cc., equivalent to 2.5 g. of sand, are measured out and placed in an 800 cc. beaker. Five cc. of hydrochloric acid (1.19) are added and the solution is diluted to 450 cc. This is stirred and 15 cc. of sodium pyrophosphate solution (25 g. in 500 cc.) are slowly added. It is then heated to boiling, stirring[2] when near the boiling point, and is boiled gently for five minutes, after which it is allowed to stand for five or ten minutes and is then filtered. The precipitate[3] is washed several times with hot water containing one or two drops of hydrochloric acid in 200 cc. It is next transferred to a 250 cc. Kjeldahl flask, and 15 cc. of sulfuric acid (1.84) and a few crystals of ammonium perchlorate are added. The flask is covered with a watch glass held away from the top of the flask by three bent pieces of glass rod. The mixture is heated until it changes to a clear brown liquid. More perchlorate is then added and heating is continued until the organic matter is all oxidized.[4] The sulfate is always slightly yellow. The mixture is cooled to room temperature. The cover glass and rods are rinsed off into the sodium hydroxide solution used in converting the sulfate to hydroxide. The flask is placed in cold water, and about 100 cc. of distilled water are slowly added with stirring, and the sulfate will soon dissolve.[5] The solution is rinsed into a solution

[1] This may be determined by placing a small portion of the mass on a watch glass, cooling, adding water and examining the undecomposed mineral fragments with a magnifying glass. The characteristic appearance of undecomposed monazite can be readily recognized.

[2] As a rule, after boiling begins, no attention is required, as the precipitate does not tend to settle.

[3] This precipitate contains about 15 mg. of oxides of rare earth elements other than thorium and zirconium.

[4] The oxidation of the filter paper requires about ten or twelve minutes, and about 1.5 g. of ammonium perchlorate are used. A larger amount of perchlorate is not harmful. Heating should be discontinued promptly when the organic matter has all been oxidized; if heated much longer, the perchloric acid breaks up at a certain point, causing considerable foaming.

[5] In the case of one of our monazites, a small amount of a greenish blue powder failed to dissolve on adding water. This occurred several times. In each case when this happened, the final result was a few one-hundredths of a per cent too low, as the precipitate contained some thorium. The following method easily overcame this

of 30 g. of sodium hydroxide in about 125 cc. of water contained in a 600 cc. beaker. The mixture is stirred and boiled for several minutes, and the hydroxide is then filtered on a hardened paper by aid of suction. It is washed a number of times with hot water. The paper is then placed in the beaker previously used, ten cc. of hydrochloric acid (1.19) are added and allowed to remain in contact with the paper for a short time, about 150 cc. of water are added and the solution is boiled. The paper is filtered off and washed, and the filtrate is diluted to 400 cc. About 3 cc. of saturated sulfurous acid solution are added, the solution is heated to boiling, and the thorium is again precipitated with sodium pyrophosphate; the precipitate is washed and changed to sulfate and hydroxide in the manner just described. This second sulfate is white and always dissolves completely in water. Finally the hydroxide is dissolved in 5 cc. of concentrated hydrochloric acid, the solution is diluted and boiled, the paper is filtered off, and the thorium is precipitated from the filtrate by a solution of 2 g. of oxalic acid. The solution is diluted to about 450 cc., and is allowed to stand warm over night. The oxalate is then filtered, washed with water very faintly acidified with hydrochloric acid, and is ignited to the oxide.

To determine the accuracy of the results, they were compared with those obtained by carefully carrying out the iodate method. The sand is decomposed and the solution made up in the manner previously described. 100 cc., corresponding to a 5 g. sample, are measured out, 50 cc. of concentrated nitric acid added, and the mixture cooled by placing in cold water. A solution of 15 g. of potassium iodate in 50 cc. of concentrated nitric acid and 30 cc. of water is added, this solution having been previously cooled. The mixture is stirred frequently and allowed to stand for one-half hour. It is then filtered.[1] The beaker is rinsed out with a solution of 4 g. of potassium iodate in 100 cc. of dilute nitric acid and 400 cc. of water. The same filter paper is used throughout the analysis. When the solution has all drained through, the precipitate is washed into the beaker with the iodate washing solution. It is stirred with about 100 cc. of this solution and filtered again. Any lumps of precipitate are pressed out with a spatula. The precipitate is now rinsed from the paper into the beaker with hot water. The mixture is heated to boiling, and the precipitate is dissolved by the addition of 30 cc. of concentrated nitric acid. The iodate is reprecipitated by a solution of 4 g. of potassium iodate in a

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difficulty: The precipitate was filtered on a small paper, washed a few times, and with the paper put in a small flask. The paper was oxidized and the precipitate brought into solution by heating with 5 cc. of concentrated sulfuric acid and a little ammonium perchlorate. After cooling and diluting with water, the solution was made alkaline with sodium hydroxide and added to the main solution containing the precipitate of thorium hydroxide.

[1] A 15 cm. S. and S. filter paper, No. 589, is recommended.

little hot water and dilute nitric acid, the solution being fully cooled before filtering, After filtering, the precipitate is again transferred to the beaker with the washing solution and is filtered once more. The precipitate is then washed from the paper with water, and the iodate is dissolved in hydrochloric acid with the aid of sulfurous acid.[1] The thorium is precipitated from the boiling solution by ammonium hydroxide, the hydroxide washed with boiling water until free from iodide, dissolved in dilute hydrochloric acid, and precipitated with an excess of oxalic acid. The oxalate is allowed to stand, filtered, washed, and ignited.

Three monazite sands were analyzed by both of these methods, and the results were found to check very closely:

MONAZITE D.		MONAZITE E.		MONAZITE F.	
Pyrophosph. meth.	Iodate meth.	Pyrophosph. meth.	Iodate meth.	Pyrophosph. meth.	Iodate meth.
5.42%	5.43%	5.70%	5.68%	5.32%	5.37%
5.41	5.43	5.70	5.68	5.34	5.34
5.41	5.50[2]	5.68	5.69	5.35	5.32
5.40		5.66	5.64	5.28	5.30
5.41		5.67	..	5.35	5.36
.		..	..	..	5.39
..		..	..	..	5.29

The oxide obtained in the pyrophosphate method was in all cases white. About 200 mg. of this oxide were fused with potassium pyrosulfate, and the melt was dissolved in water and dilute nitric acid. This solution gave no test for phosphate. Another sample of the oxide was dissolved in the same way and tested for cerium by neutralizing the solution, adding an excess of potassium carbonate solution until the soluble potassium thorium carbonate was formed, and then adding a little hydrogen peroxide. No color was obtained.

The pyrophosphate method can be completed in as short a time as either of the two rapid methods. Starting with the filtered sulfuric acid solution of the sand, all of the operations up to the precipitation of the oxalate can be carried out in about seven hours. The short time required and the cheapness of the reagents should make this a useful method for this important determination.

The monazite sands and several of the rare earth salts used in this investigation were furnished us through the courtesy of H. S. Miner of the Welsbach Company.

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[1] We have found it best to heat with dilute hydrochloric acid and add the sulfurous acid a little at a time until just enough has been added to reduce the iodate. If too much is added, the hydroxide filters slowly.

[2] This oxide had a fairly strong pink tinge, while the other oxides were white.

NOTE.

A Silver Plated Copper Gauze Electrode in the Zinc Determination.[1]—A silver plated copper gauze electrode can be made cheaply and is a good substitute for platinum in the electrolytic deposition of zinc, especially when alkaline cyanide solutions are employed. Copper gauze of a desirable mesh is cut to a convenient size, the ends are brought together to form a cylinder and all the edges folded down. The ends are joined by interlocking folds. The spiral is supported by means of a heavy copper wire which encircles the cylinder within the upper fold and is bent at right angles for connection to the support. The folds are then sewed together by means of a copper wire. The cylinder and rod are now immersed in a dilute cyanide silver bath and coated with silver by electrolysis, after which the unplated portion of the rod is cut off. A platinum wire is used for the anode connection. After each analysis, the zinc can be removed conveniently by the use of dilute hydrochloric acid.

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THE EXISTENCE OF FREE RADICALS.[2]

By M. Gomberg

Received March 31, 1914.

I. Introduction.

From the time when Kekulé and Franchimont first prepared triphenylmethane, numerous attempts were made to prepare the analogous hydrocarbon, tetraphenylmethane, but seemingly without success. Victor Meyer then suggested that the general hypothesis of steric hindrance might be applied in this case in order to explain the apparent non-existence of tetraphenylmethane: *i. e.*, three phenyl groups take up so much space around the central carbon atom that there is no room left for a fourth so complex group as a phenyl. Soon after this explanation was given, it fell to my lot to work out a method[3] by means of which a hydrocarbon, supposedly tetraphenylmethane, was produced. It turned out to be quite stable, melting in the neighborhood of 300° and distilling undecomposed at 430°. In order to obtain more evidence as to the constitution of this hydrocarbon, an attempt was made to prepare for comparative study the next higher completely phenylated hydrocarbon, hexaphenylethane, which would be similarly constituted and for that reason possess properties presumably similar to those of tetraphenylmethane. Accordingly, triphenylchloromethane was subjected to the action of metals—sodium, silver, mercury, zinc—with the full expectation that the reaction would proceed normally and give rise to hexaphenylethane:[1]

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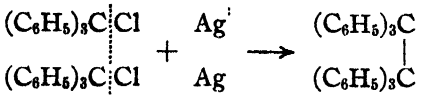
[1] See also Frary, *J. Ind. Eng. Chem.*, 5, 739, quoting L. A. Stenger.

[2] A paper read before the New York Section of the American Chemical Society, on the occasion of the presentation of the William H. Nichols Medal, March 6, 1914.

[3] *Ber.*, 30, 2043 (1897); This Journal, 20, 773 (1898).



$$\begin{array}{l} (C_6H_5)_3C \vdots Cl \\ (C_6H_5)_3C \vdots Cl \end{array} + \begin{array}{l} Ag \\ Ag \end{array} \longrightarrow \begin{array}{c} (C_6H_5)_3C \\ | \\ (C_6H_5)_3C \end{array}$$

A hydrocarbon possessing the requisite composition ($C = 93.8\%$ $H = 6.2\%$) was actually obtained. But the unusual instability of this substance, its proneness to enter into most varied chemical reactions, and above all, its strikingly unsaturated character, precluded the natural inference that the hydrocarbon at hand was actually hexaphenylethane. The opinion was expressed that here was an instance of a compound with one atom of carbon in the trivalent state, *i. e.*, $(C_6H_5)_3C$, *triphenylmethyl*, a free radical. Subsequently it was found that many analogs of triphenylmethyl are capable of existence. In other words, there is a large class of such free radicals, a class of *triarylmethyls*.

A brief description of the most important properties of this strange class of compounds and a discussion of the arguments that have been advanced for and against the conception of free radicals will be the subject of my talk before you.

II. The General Reaction.

The mother substance is the hydrocarbon triphenylmethane, a colorless, fairly stable compound. By bromination we obtain triphenylbromomethane, a derivative of great activity. This bromide, and the analogous chloride, resemble in their general behavior the acid halides more than the alkyl halides. The halogen is easily replaced by other groups, and we may obtain a carbinol, an ether, an amine, an anilide, etc., all tolerably stable and all colorless compounds. What is true of the triphenylmethane is equally true of other triarylmethanes.

When a triarylmethylhalide, dissolved in benzene, is treated with some metal, like silver, in absence of oxygen the halogen is taken out by the metal and the unsaturated triarylmethyl is formed. The solution is invariably colored. The exact nature of the color so produced is dependent upon the nature of the three groups that are linked to the carbon atom. The triphenylmethyl itself gives in solution, as you notice, an orange-yellow color. But colors corresponding to all shades of the rainbow can be obtained by varying the nature of the three aryl groups in union with the central carbon atom. Let me illustrate this on the following triarylmethyl chlorides, to each of which some molecular silver has been added.

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[1] This Journal, 22, 757 (1900); *Ber.*, 33, 3150 (1900).

(1) $(C_6H_5)_3C.Cl$ gives an orange-yellow solution.[1]
(2) $(C_6H_5)_2.(p\text{-}CH_3C_6H_4).C.Cl$ gives an orange-red solution.[2]
(3) $(p\text{-}CH_3.C_6H_4)_3C.Cl$ gives a darker red solution.[3]
(4) $(p\text{-}BrC_6H_4).(C_6H_5)_2.C.Cl$ gives a brown-red solution.[4]
(5) $(o\text{-}BrC_6H_4)(C_6H_5)_2.C.Cl$ gives a red solution.[5]
(6) $(o\text{-}BrC_6H_4)(p\text{-}C_6H_4Cl)_2C.Cl$ gives a purple-red solution.[5]
(7) $(C_6H_5)_2.(\alpha\text{-}C_{10}H_7).C.Cl$ gives a dark brown solution.[6]
(8) $(p\text{-}NO_2C_6H_4).(C_6H_5)_2C.Cl$ gives a deep green solution.[7]

While the production of color in itself is characteristic, the susceptibility of the colored compound to the oxidizing influence of the air is by far its most striking feature. When, therefore, any one of these solutions be exposed to air the color will disappear. Let me illustrate this by the four examples: (1), (5), (7), and (8). This test, the production of color and the disappearance of it on exposure to air, is extremely delicate, a few mgs. of the material under examination suffice for the test.

III. Preparation of the Pure Triarylmethyl.

In order to prepare a triarylmethyl pure, the essential conditions are: (1) exclusion of moisture, to prevent the hydrolysis of the triarylmethyl halide itself; (2) absence of oxygen, to prevent the oxidation of the resulting unsaturated hydrocarbon; (3) avoiding exposure of the solutions to light—especially direct sunlight—to prevent autoöxidation; (4) avoiding even traces of acids, to prevent isomerization. Various contrivances can of course be used in order to insure the above conditions. Schmidlin, Schlenk and others have each described an apparatus answering these demands. The form of an apparatus which we have employed in our own laboratory, with very satisfactory results, was described some years ago.[8] It permits of the preparation, recrystallization, filtration, washing and drying of the final product without ever exposing it to the oxidizing influence of the air.

IV. Physical Properties of Triphenylmethyl.

Color.—The simple representative—triphenylmethyl itself—is in the solid state undoubtedly colorless, but it invariably becomes covered with a thin yellow coating, even if completely protected from the oxygen of the air. On the other hand, as the writer has demonstrated and has repeatedly called attention to the fact, the colorless triphenylmethyl goes into solution with the production of a distinct orange-yellow color in any solvent whatsoever. We must conclude that the compound, in dissolving, must undergo a change in molecular structure and that there are two modifications of triphenylmethyl, colorless and colored.[1] The credit belongs to Schmidlin[2] to have established by experiment that, even in solution, both modifications—the colorless and the yellow—exist side by side, in equilibrium with each other. There have been proposed several hypotheses in order to explain the difference in constitution between the colorless and the colored modification. We shall discuss them later.

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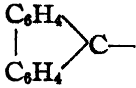
[1] Gomberg, This Journal, 22, 757 (1900); *Am. Chem. J.*, 25, 320 (1901).
[2] Gomberg, *Ber.*, 37, 1631 (1904).
[3] *Ibid.*, 37, 1627 (1904).
[4] *Ibid.*, 37, 1635 (1904).
[5] Gomberg and Van Slyke, This Journal, 32, 540 (1911).
[6] Gomberg, *Ber.*, 37, 1637 (1904).
[7] To be described in detail later.
[8] *Ber.*, 37, 2033 (1904).

That various analogous triarylmethyls may possess other than yellow color has already been called attention to. Some are colored even in the solid state. There is one hydrocarbon of this class,  $\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right>C—C_6H_5$, which is colorless even in solution, but on heating, the solution assumes a deep blue fluorescence, almost as blue as the color of copper sulfate.

Stability.—Triphenylmethyl, in the solid state, can be kept indefinitely. Samples sealed up in an atmosphere of carbon dioxide were found to be unimpaired on opening after having been kept five years. Triphenylmethyl melts at 145°. On distilling at 18 mm. pressure it decomposes, producing considerable quantities of triphenylmethane. With a better vacuum it may prove possible to distil it undecomposed.

Solvents of Crystallization.—The unsaturated character of triphenylmethyl is evidenced by its avidity to unite with a variety of solvents.[3] In fact, it is difficult to find solvents from which triphenylmethyl can be crystallized without its taking up solvent of crystallization. It unites with benzene, toluene, the three xylenes, ethyl benzene; with methylethyl ether, diethyl ether, methylpropyl ether, ethylpropyl ether, methylal anisol, benzylethyl ether, *o*-cresolmethyl ether, methylene oxide, etc.; with ketones, such as methylethyl ketone, diethyl ketone, methylpropyl and ethylpropyl ketone, acetyl acetone, methylhexyl ketone, acetophenone, etc.; with aldehydes;[4] with esters, such as formates, acetates, propionates, butyrates, carbonates, oxalates, malonates, succinates, benzoates, etc.; it unites with nitriles, with CS_2, with chloroform, with olefines. Particularly puzzling is the fact that when crystallized from petroleum ether the crystals so obtained contain actually petroleum ether of crystallization. Samples of American petroleum ether and of Kahlbaum ether, thoroughly washed with nitric acid and then with potassium permanganate, still give combinations with triphenylmethyl containing 14–15% of petroleum ether. We are at present investigating whether synthetic hexane, heptane, etc., are taken up by triphenylmethyl.

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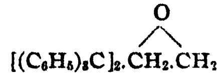
[1] *Ber.*, 34, 2728 (1901); 35, 1825, 2403 (1902).

[2] *Ibid.*, 41, 2471 (1908).

[3] Gomberg, THIS JOURNAL, 23, 496 (1901); Gomberg and Cone, *Ber.*, 38, 1333, 2447 (1905); and some unpublished results.

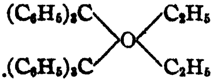
[4] From results obtained by R. L. Jickling, in this laboratory, both aliphatic and aromatic aldehydes combine with triphenylmethyl.

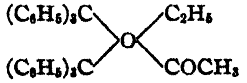
The combinations which are so formed are easily dissociated into the components near or at the boiling points of the respective solvents. The constancy and uniformity of composition is very striking, as can be seen from examples in the following table:

Aromatic hydrocarbon:	$[(C_6H_5)_3C]_2.C_6H_6$
Ether:	$[(C_6H_5)_3C]_2.(C_2H_5)_2O$
Ketone:	$[(C_6H_5)_3C]_2.CH_3\,CO.C_2H_5$
Aldehyde:	$[(C_6H_5)_3C]_2.C_6H_5CHO$
Ester:	$[(C_6H_5)_3C]_2.CH_3COOR$
Nitrile:	$[(C_6H_5)_3C]_2.C_2H_5CN$
Olefine:	$[(C_6H_5)_3C]_2.C_6H_{12}$
Ethylene oxide:	 $[(C_6H_5)_3C]_2.\overset{O}{CH_2.CH_2}$

It is purely an incident that among the ketones, acetone, and among the esters, methyl- and ethyl-formate, do not give combinations with triphenylmethyl. It is more likely true that these solvents also combine with the hydrocarbon, but the temperature of dissociation lies very low, below ordinary room temperature.

From the constancy of composition it was at first inferred that these combinations occur, or are formed, in virtue of the tetravalency of the oxygen:





Lately, however, our studies have forced us to the conclusion that the assignment of constitutions with tetravalent oxygen to different compounds by various investigators was based in most cases upon erroneous and faulty experimental evidence. For this reason we would hesitate to defend our former point of view as regards the constitution of compounds produced by the combination of triphenylmethyl with ethers, ketones, esters, etc.

Conductivity.—Early in the development of this subject it became apparent that triphenylchloromethane, and also other triarylchloromethanes possess characteristics not unlike those of salts: they make perbromides, periodides, give double salts with metal halides,[1] etc. If salts—are they capable of conducting the electric current? Of course water could not be used as the solvent in this test, since the carbinol halides are readily hydrolyzed by it to the carbinols. Organic solvents known to possess more or less dissociating power were tried. Triphenylchloro- and bromomethane showed a measureable, but rather slight, conductivity in benzonitrile; in nitrobenzene, still less. Liquid sulfur dioxide was next employed, which, as you know from Walden's work, is as good an ionizing solvent for both inorganic and organic electrolytes as water itself. Walden[1] and we[2] in our laboratory, in Riga, found that these triarylmethyl halides behave truly like salts, in that they show a conductivity equal to that of ethylamine, benzylamine; moreover, the molecular conductivity increases with dilution. It was thus definitely established that there are "*carbonium*" salts in the true sense of the definition applied to salts. The conclusion was tentatively drawn that the basic properties, in virtue of which the salt formation occurs, reside in the central carbon atom. This conclusion is still held by some, but we shall see later why this interpretation was given up in favor of another which appears to us to be more in conformity with the facts.

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[1] Norris and Sanders (*Am. Chem. J.*, 25, 55 (1901)) described the first double salt of this kind, namely, the aluminum chloride double salt. Soon after that, the writer prepared a number of analogous double salts from triphenyl- and tritolyl-chloromethane, with various metal halides (This Journal, 23, 496 (1901); *Ber.*, 34, 2727 (1901)). Following this, Kehrmann and Wentzel described other double salts of this nature (*Ber.*, 34, 3818). Since then, large numbers of these derivatives have been described by various investigators.

But, however, far more surprising than the apparent existence of the carbonium salts is the unexpected discovery that triphenylmethyl itself behaves exactly like an electrolyte when dissolved in liquid sulfur dioxide.[3] It, too, conducts the electric current quite well. It, too, possesses a higher molecular conductivity the more dilute the solution.

How is this strange phenomenon, a hydrocarbon behaving like an electrolyte, to be accounted for? Several explanations have been offered, but none of these is entirely satisfactory.

V. Chemical Properties.

Oxidation.—Foremost among the chemical reactions of triphenylmethyl, and all its analogs, is the readiness with which they unite with oxygen. We have seen this illustrated when the colored solutions of the various triarylmethyls lost their color on exposure to air. Permit me to illustrate this striking characteristic again, emphasizing this time the unusual *rate* of oxidation. On exposing to air a concentrated solution of triphenylmethyl in benzene (10%), it will be noticed that the clear solution in a very short time becomes covered with a crust of the insoluble oxidation product. The rate of absorption of oxygen is 50 cc. per 1 g. of material during the first minute of exposure.[4] Yellow phosphorus hardly exceeds triphenylmethyl in the rate with which the latter unites with the oxygen of the air.

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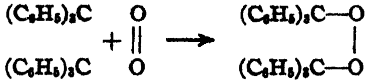
[1] *Z. physik. Chem.*, **43**, 454 (1903).

[2] *Ber.*, **35**, 2404 (1902); Tousley and Gomberg, THIS JOURNAL, **26**, 1516 (1904).

[3] Walden, *Z. physik. Chem.*, **43**, 443 (1903); Gomberg and Cone, *Ber.*, **37**, 2043 (1904).

[4] Gomberg and Cone, *Ber.*, **37**, 3540 (1904).

The compound formed in this reaction is a colorless, fairly stable substance and it has the constitution of a peroxide:



$$\begin{array}{l} (C_6H_5)_3C \\ (C_6H_5)_3C \end{array} + \begin{array}{c} O \\ \| \\ O \end{array} \longrightarrow \begin{array}{l} (C_6H_5)_3C{-}O \\ \qquad\quad | \\ (C_6H_5)_3C{-}O \end{array}$$

These peroxides, as a rule, are comparatively little soluble in the usual organic solvents such as benzene and ether, and thus their purification presents no difficulties. Consequently, the isolation of a peroxide in a reaction as described is positive proof that a compound containing a trivalent carbon atom is present. By the employment of this simple test we have proven the existence of a large number of free radicals.

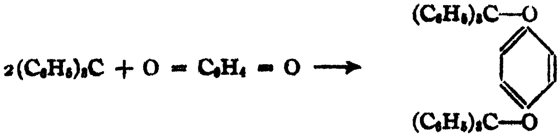
Addition of Iodine.—Next to the combination with oxygen, the behavior of triphenylmethyl towards halogens is very striking. It unites instantly with bromine, with chlorine, the reaction consisting in both substitution as well as addition. But with *iodine*, addition only takes place. Let me illustrate this by adding a solution of iodine in benzene to a similar solution of triphenylmethyl, and you notice that the dark color of iodine disappears instantly. Triphenylmethyl may be titrated in this manner with a standard solution of iodine.[1] In this reaction there is formed triphenylmethyliodide:

$$(C_6H_5)_3C + I \longrightarrow (C_6H_5)_3C{-}I.$$

Addition of Hydrogen.—As might be expected, triphenylmethyl adds hydrogen with the greatest ease, forming triphenylmethane. The hydrogenation can be carried out by adding a little zinc dust and some acetic acid[2] to a benzene solution of the unsaturated hydrocarbon. Or, in presence of finely divided platinum, hydrogen, as such, readily converts triphenylmethyl to triphenylmethane.[3]

$$(C_6H_5)_3C + H \longrightarrow (C_6H_5)_3CH.$$

Addition of Quinone.—Schmidlin[4] found that triphenylmethyl combines readily with quinone, giving stable compounds. He assigned to them the constitution:



Addition of NO and NO₂.—Schlenk and Mair[5] found that the oxides of nitrogen are taken up by triphenylmethyl with the greatest avidity. The products formed are nitroso- and nitrotriphenylmethane.

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[1] This Journal, 24, 597 (1902); *Ber.*, 35, 1822 (1902).

[2] *Ber.*, 36, 381 (1903).

[3] Schmidlin u. Garzia-Banus, *Ibid.*, 45, 3190 (1912).

[4] *Ber.*, 43, 1298 (1910).

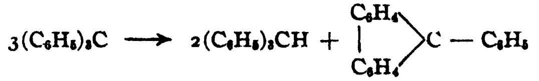
[5] *Ibid.*, 44, 1170 (1911).

$$2(C_6H_5)_3C + NOCl \longrightarrow (C_6H_5)_3C{-}NO + (C_6H_5)_3CCl$$
$$(C_6H_5)_3C + NO_2 \longrightarrow (C_6H_5)_3C.NO_2.$$

Addition of Xylene.—Wieland and Müller[1] recently reported interesting results regarding the capacity of triphenylmethyl to combine with aromatic hydrocarbons in a way different from merely taking them up as solvents of crystallization. Wieland found that, on heating triphenylmethyl with xylene, dimethyltetraphenylmethane is formed:

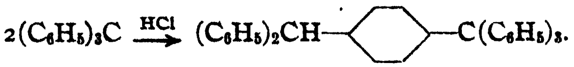
$$2(C_6H_5)_3C + C_6H_4(CH_3)_2 = (C_6H_5)_3C.C_6H_3(CH_3)_2 + (C_6H_5)_3CH.$$

Action of Light.—Solutions of triphenylmethyl in benzene are quite susceptible to light, especially direct sunlight.[2] Like most photochemical processes of this type, the reaction in this instance also is autoöxidation and reduction. Schmidlin[3] showed that the following reaction takes place:



$$3(C_6H_5)_3C \longrightarrow 2(C_6H_5)_3CH + \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!C - C_6H_5$$

Action of Acids.—Hydrochloric acid, and undoubtedly other acids, exert a peculiar catalytic influence upon triphenylmethyl. The unsaturated, unstable hydrocarbon is thus converted, in the presence of small quantities of acids, into an isomeric stable hydrocarbon.[4] This hydrocarbon was first prepared by Ullmann and Borsum[5] directly from triphenylchloromethane, and later by the writer from triphenylmethyl as mentioned above. It was first taken for the true stable hexaphenylethane. But Chichibabin[6] definitely proved its constitution to be that of *p*-benzhydryltetraphenylmethane:



Triphenylmethyl reacts also with phenols,[7] with diazomethane,[8] with substituted hydrazines,[9] etc. It may be mentioned, however, that it *does not* unite with cyanogen, nor with CO.[10]

[1] *Ann.*, **401**, 238 (1913).

[2] Gomberg and Cone, *Ber.*, **37**, 3546 (1904).

[3] *Ber.*, **45**, 1345 (1912).

[4] *Ibid.*, **35**, 3914 (1902); **36**, 376 (1903).

[5] *Ibid.*, **35**, 2877 (1902).

[6] *Ibid.*, **37**, 4708 (1904); **41**, 2422 (1908).

[7] Schmidlin, *Ber.*, **45**, 3180 (1912); Gomberg and Cone, *Ibid.*, **37**, 2040 (1904).

[8] Schlenk u. Bornhardt, *Ann.*, **394**, 183 (1912).

[9] Wieland and Lecher, *Ibid.*, **381**, 214 (1911).

[10] Gomberg, THIS JOURNAL, **22**, 762 (1900).

VI. Constitution, First Period, 1900–1905.

Associated State.—It is obvious that the entire chemical behavior of triphenylmethyl finds its most consistent and most plausible explanation in the hypothesis that this hydrocarbon is a free radical containing a trivalent carbon atom. This explanation when first advanced was received without open opposition, but none the less with hesitancy, notwithstanding the fact that the extensive investigations by Nef have prepared us for the variability of the valence in carbon. The hesitation to acquiesce in the hypothesis of the trivalency of carbon received later its main support from the fact that the molecular weight of triphenylmethyl was found to be not 243, but double that. We used (1904) for the determination of the molecular weight by the cryoscopic method a wide range of solvents, freezing at various temperatures between 5° and 80°; such solvents as benzene, nitrobenzene, dimethylaniline, bromotoluene, phenol and naphthalene. Only in naphthalene did the molecular weight of triphenylmethyl drop considerably below 486, namely, to 410.

Here, then, was the dilemma: The entire chemical behavior of the unsaturated hydrocarbon speaks forcibly, almost exclusively, in favor of the trivalency of carbon. The only argument against this interpretation is the dimolecular state of the compound, one single physical constant. It did not seem, however, impossible to reconcile this apparent contradiction between the molecular weight, on the one hand, and the entire chemical behavior of the compound on the other hand. We have numerous examples among inorganic, as well as organic compounds, where substances in solution possess abnormally high molecular weights, double and triple that demanded by the composition and constitution of the compound in question. We say, under such circumstances, that the substance exists in the associated state, *i. e.*, several molecules unite to form a single aggregate. Is it not possible that triphenylmethyl, whatever be its molecular weight in the solid state, exists in solution in the associated state as dimolecular? Is not water itself polymolecular, the size of the aggregate varying with the temperature? Are not the organic nitriles, the acids, the acidamides di- or poly-molecular in solution? Is not association favored by the unsaturated state of the compound in question? And is not the associated state preëminently favored by solvents which lack the ionizing power, such, for instance, as the usual organic solvents? Why, then, may it not be assumed that triphenylmethyl is, perchance, in the associated state, *i. e.*, dimolecular? To quote from a paper of ten years ago:[1] "The depressions in the freezing point obtained with naphthalene as a solvent at the elevated temperature of 79–80° suggest the probability that at this temperature triphenylmethyl exists partially in the dissociated monomolecular state, as the molecular weights in this solvent are 407–420 as against 486 in other solvents. On the assumption that such dissociation may exist, be it to ever so small an extent, the behavior of the hydrocarbon becomes intelligible: through the action of oxygen or of iodine, the monomolecular form reacts first, the equilibrium is thus disturbed and it can only be restored through further and further dissociation of the dimolecular triphenylmethyl until all the compound has reacted."

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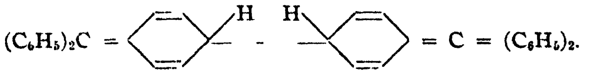
[1] *Ber.*, 37, 2049 (1904).

$$\underset{\text{Solid}}{(R_3C)_n} \longrightarrow \underset{\text{Solution}}{(R_3C)_2} \rightleftharpoons R_3C.$$

Dimolecular Formulae.—The dimolecular state of the hydrocarbon was, however, the occasion for the suggestion of various structures for triphenylmethyl, all intending to do away with the interpretation involving the existence of free radicals.

(1) Markownikoff,[1] in 1902, expressed the opinion that "triphenylmethyl" is in reality hexaphenylethane. Assuming the latter to be extremely unstable, we can account for its decomposition reactions, by oxygen, by iodine, etc. But on what to base the assumption that hexaphenylethane must be unstable? How to account for it? No explanation was offered.

(2) Heintschel,[2] in 1903, suggested that the dimolecular state of the so-called triphenylmethyl, as well as its yellow color in solution, can be explained, perhaps, by the following formula:



(3) Vorländer,[3] in 1904, suggested that triphenylmethyl, dimolecular, must in some way be different from the actual hexaphenylethane, which, if prepared, would turn out to be stable, he believed. And so Vorländer put forward the indefinite notion of two isomers:

$[(C_6H_5)_3C]_2$	$(C_6H_5)_3C — C(C_6H_5)_3.$
Bistriphenylmethyl, hexaphenylethane A, unstable	Hexaphenylethane B, stable.

It is indeed difficult to see the difference between this explanation and the notion of molecular combination or association

(4) Chichibabin,[4] in 1904 and 1905, came to the defense of the hexaphenylethane constitution. He, like Markownikoff, insisted that hexaphenylethane may be expected to be extremely unstable, readily decomposable, and consequently the triphenylmethyl is in reality nothing more than hexaphenylethane. Among the arguments adduced by Chichibabin

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[1] *J. Russ. Phys. Chem. Soc.*, **34**, 140 (1902).

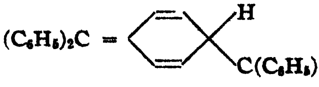
[2] *Ber.*, **36**, 320 (1903).

[3] *Ann.*, **341**, 1 (1905); **348**, 155 (1906).

[4] *Ber.*, **37**, 4708 (1904); *J. prakt. Chem.*, **74**, 340 (1906).

in favor of this view was the well-known instability of trimethylene and its homologs, and other similar analogies. The fact that the saturated compound triphenylmethyl iodide gives triphenylmethyl peroxide on exposure to air appeared of particular significance to Chichibabin. Why then, said Chichibabin, could not *hexaphenylethane*, also saturated, give under similar conditions the peroxide? Chichibabin became a vigorous advocate of the hexaphenylethane formula.

(5) Jacobson,[1] 1905, disagrees with Chichibabin, and assigns to triphenylmethyl the following constitution, which is not unlike Heintschel's, a quinol-like constitution:



And, indeed, many of the reactions of triphenylmethyl are not unlike those of quinols.

(6) Flürscheim[2] (1905) thought it is hexaphenylethane, unstable, partly broken down into R_3C.

Thus, then, stood the question of the constitution of triphenylmethyl at the end of 1905. Leaving out Heinstchel's formula, there was in the field: (1) The idea of the associated molecule, associated but none the less in equilibrium with the monomolecular free radical; (2) the hexaphenylethane formulation, based upon the assumption that this, unlike all other saturated hydrocarbons, is, or rather ought to be, extremely unstable; (3) Jacobson's quinol formula. Each of these three explanations had followers, but undoubtedly the "free radical" idea was most favored, and was most widely adopted.

VII. Constitution, Second Period, 1905-1910.

We now enter upon the second period of our hypothesis. These questions presented themselves: Is it possible to show by *experimental* evidence whether a hydrocarbon of the type of hexaphenylethane *is* or *is not* stable? Is it possible to test experimentally the validity of Jacobson's suggestion? Upon the nature of the answers to these two questions the acceptance or the rejection of the hypothesis relative to the existence of free radicals depended. Let us follow each line of the inquiry separately.

Phenylated Ethanes.

One of the fundamental arguments in favor of the probable instability of hexaphenylethane was the well-known fact that the unsymmetrical tetraphenylethane seemed impossible of preparation. Anschütz[3] proved definitely that all methods, perfectly logical and reasonable in themselves, which have been employed by the many investigators to obtain the unsymmetrical tetraphenylethane, invariably resulted in giving the *symmetrical* compound.

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[1] *Ber.*, 38, 196 (1905).

[2] *J. prakt. Chem.*, 71, 505 (1905).

[3] *Ann.*, 235, 150 (1886).

$$(C_6H_5)_3C - CH_2(C_6H_5); \qquad (C_6H_5)_2CH - CH(C_6H_5)_2.$$

Unsymmetrical tetraphenylethane. Symmetrical tetraphenylethane.

The conclusion became prevalent that the unsymmetrical hydrocarbon could not exist, owing to its instability. The cause of such instability was implied to be of the same nature as that of the supposed instability of tetraphenylmethane, namely, the lack of capacity on the part of a carbon atom to hold more than three complex groups. From the presumed instability of the unsymmetrical tetraphenylethane it was further surmised that the more complex hydrocarbons, pentaphenyl- and hexaphenylethane, may reasonably be expected to be still more unstable and, consequently, less likely to exist as such.

In an attempt to improve upon the original method of the synthesis of tetraphenylmethane, it occurred to Dr. Cone and myself[1] to apply the Grignard reaction, being unaware, because of the very brief mention in the *Chemiker Zeitung* only, that Freund and Beck[2] had used the same reaction just previous to us:

$$(C_6H_5)_3CCl + BrMgC_6H_5 = (C_6H_5)_3C.C_6H_5 + MgClBr.$$

The reaction proceeded as expected, but the yield of the desired hydrocarbon was very unsatisfactory. Again we explained the result to ourselves by the hazy, but none the less useful notion of steric hindrance, *i. e.*, there is but little room left around the same carbon atom for the fourth phenyl group. In order to test the plausibility of this explanation, it was decided to couple triphenylchloroethane with magnesium benzylchloride, placing, in this manner, the fourth phenyl group at a further distance from the central carbon atom.

$$(C_6H_5)_3C.Cl + ClMgCH_2C_6H_5 = (C_6H_5)_3C.CH_2C_6H_5 + MgCl_2.$$

It was indeed a most welcome surprise that this reaction did proceed, and almost quantitatively, too. We were able to obtain any amount of the long-sought-for hydrocarbon. It turned out to be a very stable substance, beautifully crystalline, distilling in a vacuum at 270–280° unchanged, and was oxidized with considerable difficulty by CrO_3. All in all, this hydrocarbon showed no resemblance to triphenylmethyl. Moreover, a revision of some of the methods that have been previously employed by others,[3] and have been reported as unsuitable, convinced us that several investigators have actually had this hydrocarbon in their hands, but through lack of proper purification did not recognize it as such.

The next step was to prepare pentaphenylethane. Here a number of difficulties were encountered. But finally this hydrocarbon, too, was prepared, by the action of magnesium upon a mixture of triphenylchloromethane and diphenylbromomethane:

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[1] *Ber.*, 39, 1461 (1906).

[2] *Chem. Ztg.*, 1905, 768; *Ber.*, 39, 2237 (1906).

[3] Hanriot and Saint Pierre, *Bull. soc. chim.*, [3] 1, 774 (1889).

$$(C_6H_5)_3CCl + Mg + BrCH(C_6H_5)_2 = (C_6H_5)_3C—CH(C_6H_5)_2 + MgClBr.$$

So far as we could notice at the time, pentaphenylethane presented no resemblance to the elusive triphenylmethyl. True enough, we noticed that on heating the hydrocarbon to its fusion point, 180°, some decomposition occurred. But on the other hand, we encountered no difficulty in recrystallizing pentaphenylethane from various solvents; no oxidation on exposure to air was observed.

The successful preparation of the two higher phenylated ethanes, above described, made it now seem more probable than ever that the hypothetical hexaphenylethane ought also to be a *stable* compound and that it also could be prepared if only the conditions requisite for this process could be found. Alas, neither we nor anyone else of the many who have tried it have till this day found the requisite conditions. Hexaphenylethane still remains a figment of the imagination. And so the idea began to take root more and more generally that, after all, there is no difference between the so-called triphenylmethyl and the hexaphenylethane, that the former is in reality the latter. Add to this the insistent emphasis which Chichibabin[1] laid upon his discovery that pentaphenylethane is, after all, not so very stable, that it is decomposed by hydrochloric acid at 150°, and that it absorbs oxygen at its melting point, at 180°—and you have at least a *formal* analogy, if not a real one, between pentaphenylethane and triphenylmethyl. That the analogy is purely formal can hardly be doubted. The difference is so great between the surpassing susceptibility of triphenylmethyl on the one hand, and the violent conditions necessary for the decomposition of the pentaphenylethane on the other hand, that one is equally justified in emphasizing the *lack* of analogy between these two hydrocarbons as the *existence* of the analogy, depending entirely upon the subjective view point.

Be that as it may, these two factors taken together, the failure to prepare a stable hexaphenylethane and the apparent lesser stability of pentaphenylethane than was attributed to it, these two factors had much to do with shaking the confidence of chemists that hexaphenylethane, as such, ought to be a stable substance and unlike triphenylmethyl. Henceforth the hexaphenylethane constitution for triphenylmethyl began to appear in the literature more frequently, at least as one of the more probable constitutions. It is self-evident that such a constitution could at best account for the *colorless* triphenylmethyl alone, the existence of the second, colored modification being explicable only with the help of some additional hypothesis.

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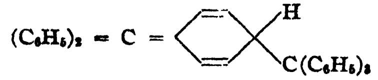
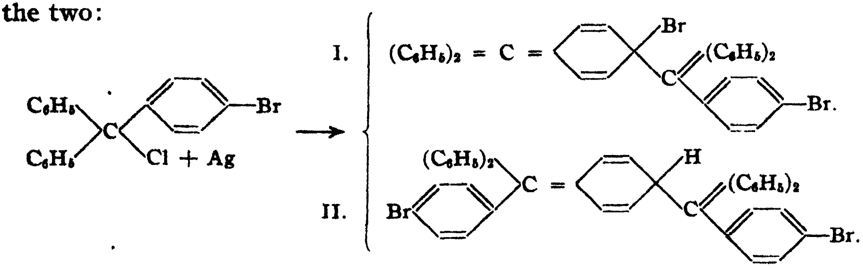
[1] *Ber.*, 40, 367 (1907). Compare also Cone and Robinson, *Ibid.*, 40, 2160 (1907); Schlenk and Herzenstein, *Ibid.*, 43, 3542 (1910); Norris, Thomas and Brown, *Ibid.*, 43, 2945 (1910).

Quinol Formula of Jacobson,



Competing with the hexaphenylethane hypothesis for recognition as the constitution of the dimolecular triphenylmethyl was the quinol formula of Jacobson, suggested in 1905. Unfortunately the author of this suggestion, like the defenders of the hexaphenylethane constitution, apparently took no cognizance of the fact, at that time well established, that there are two modifications of triphenylmethyl, the colorless and the colored. Which of these two should be represented by the quinol formula? If it be the colored modification, as was probably intended by Jacobson, how to account for the remarkable facility with which it isomerizes into the colorless modification through merely evaporating the solvent? It is an axiom with organic chemists that the presence of a "quinone" ring in the molecule imparts to the compound the attribute of the color. Whether the presence of a quinol ring may exert a similar influence was by no means certain at that time. Indeed, the known facts pointed to the contrary.[1] For this reason the writer[2] did not favor the quinol formula until after the experiments described in the following pages had clearly demonstrated that triphenylmethyl behaves as if it actually contained some kind of a quinoid nucleus. And later, when the quinol hypothesis, modified, was adopted by the writer, it was only in order to explain the constitution of the colored modification, and not of the colorless isomer.

In deciding to subject the validity of this quinoid hypothesis to the test of the experiment, we were guided by the following idea:[3] Suppose we start with the mono-*p*-bromotriphenylmethylchloride, and allow metallic silver to act upon it. On the basis of the quinol hypothesis the first step of the reaction must consist in the formation of a triphenylmethyl analog, the constitution of which, *in solution*, must be one of the two:



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[1] Zinke and Krügener, *Ann.*, **330**, 68 (1904); *Ann.*, **320**, 189 (1902).

[2] *Ber.*, **38**, 2457 (1905).

[3] Gomberg and Cone, *Ber.*, **39**, 3274 (1906); Gomberg, *Ber.*, **40**, 1880 (1907).

If there be any doubt which of these two reactions, I or II, are likely to take place, one may start with a triarylmethyl halide that contains a para bromine atom in each of the three nuclei, as has been done in later experiments. But let us consider the simple problem, when there is only one brominated nucleus, and let us assume that the quinoidation takes place exclusively in the substituted ring. It is evident that the bromine atom in the quinone nucleus must now become labile, since the stabilizing effect of the benzene or "aromatic" nucleus is now wanting. Consequently this bromine atom should be easily taken out by metallic silver. On the basis that the reaction is quantitative, it can be readily seen, the silver will remove first of all one atom of carbinol-chlorine from each molecule of bromo-triphenylchloromethane, with the subsequent formation of compound I; and now, from the latter, the silver can take out only one bromine atom, and not the two. In other words, each brominated triphenylchloromethane can in this process lose no more than one and one-half atoms of halogen, one atom of chlorine and one-half atom of bromine. Now, we have tested these presuppositions on a large number of examples, and found this rule to hold absolutely true: the amount of halogen removed, over and above the carbinol-chloride, is always $^1/_2$ atom. You will ask, what results, if the one atom of bromine in the quinone nucleus is taken out? The answer is, we get once more a compound containing a trivalent carbon atom—still an unsaturated radical—and this in its turn may combine with another like radical and give rise to a compound of similar quinoid formulation, but twice as complex. Suffice it merely to state here, that we calculated how much bromine one may expect to remove if two, and also if all three nuclei contain bromine in the para position; and the calculated amounts, $^3/_4$ and $^7/_8$ of an atom, coincided to a remarkable degree with the quantities actually found at that time. All subsequent work confirmed these results.[1]

The above results seemed convincing that a quinoid constitution of some nature for the colored modifications of triphenylmethyl must and should be taken into account. However, by themselves, these results did not suffice to prove the correctness of the quinol formula. But strong corroborative evidence was soon obtained, evidence which proved the validity of the method described above and which also made it obvious how a colorlesss modification may, through tautomeric changes, give rise to a colored triphenylmethyl. Such evidence was supplied by the study of the quinocarbonium salts.

Quinocarbonium Salts.

The probable quinoid character of triphenylmethyl threw a flood of light on many phenomena which were at that time subjects of much debate. Baeyer strenuously opposed Kehrmann's view that the colored solutions of triphenylcarbinol in strong acids are due to the formation of quinoid salts of the type II, rather than of benzoid type I.

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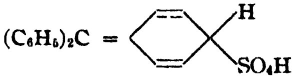
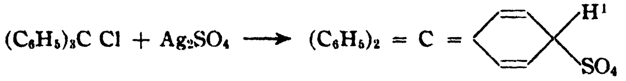
[1] *Ber.*, 39, 3294 (1906); *Ibid.*, 40, 1886 (1907); *Ann.*, 370, 181 (1909); *Ibid.*, 376, 208 (1910); Gomberg and Van Slyke, THIS JOURNAL, 32, 538 (1911).

(I) $(C_6H_5)_3C—SO_4H$ (II)

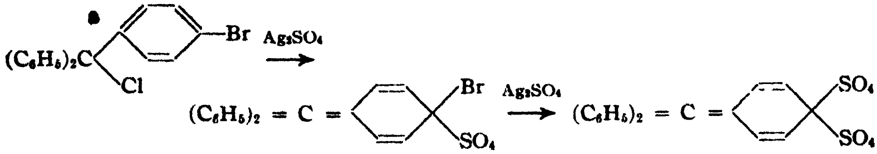


In the light of the results with triphenylmethyl our adherence to Baeyer's view began to waver. We then undertook to test the validity of these views by the same method that was employed in the case of triphenylmethyl. Contrary to Baeyer's previous findings, the verdict of our experiments was positive; these salt-like bodies were proven to be quinoid in their constitution.

When triphenylchloromethane or any of its analogs is treated with Ag_2SO_4 a double transposition takes place. Silver chloride precipitates out and triphenylmethyl sulfate is formed. This reaction is best carried out in methyl sulfate as the solvent, since the triarylmethyl sulfates are soluble in it. But, notice: while the chlorides are colorless, the sulfates resulting from them are intensely colored. This in itself is strongly suggestive that the sulfates must have a different constitution than the chlorides. And because of the color attribute the assumption is reasonable that the constitution of the sulfates is presumably quinoid.



Positive proof in regard to the quinoid character of the sulfates was found in the behavior of para-brominated triphenylmethyl chlorides. We found, namely, that when *p*-bromotriphenylcarbinolchloride is subjected to the action of Ag_2SO_4, the reaction consists in removing not only the "carbinol" chlorines, but equally so the "nucleus" bromine.[2] The interpretation can be none other than this:



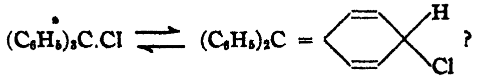
To fully appreciate the cogency of this argument in favor of the quinoid constitution of the sulfates, one must bear in mind that *p*-brominated triphenylcarbinols are entirely unaffected by Ag_2SO_4—they remain colorless and their nucleus bromine is not taken out. The sulfates, therefore, differ from the corresponding carbinols not merely in possessing color, but in acquiring at the same time a change in the brominated nucleus, a change

[1] SO_4 = one-half equivalent.

[2] *Ber.*, 40, 1847 (1907); Gomberg and Van Slyke, THIS JOURNAL, 32, 540 (1911).

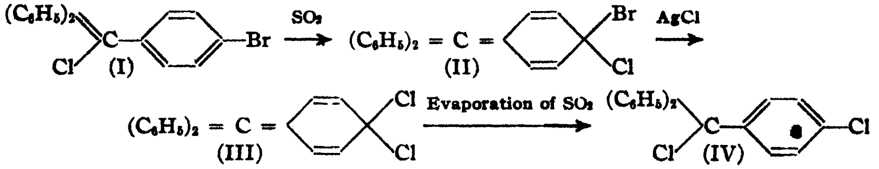
which indicates that the nucleus which contains the bromine atom has lost its stability—and is consequently no longer the true benzene nucleus.

Having thus connected positively by actual experimental evidence the color-formation of the sulfates with their simultaneous acquisition of the quinoid state, the attention was next directed to the chlorides. In the early part of this paper it has been mentioned that triphenylchloromethane and its analogs dissolve in liquid sulfur dioxide with pronounced color and behave in this solvent like true salts. On the evaporation of the solvent the original colorless chloride is again obtained. The question arose, may not the production of color be accompanied also in this instance by the conversion of the chloride while in solution in liquid sulfur dioxide, to the quinoid state:



Is it not probable that the triarylmethylchlorides may exist in two tautomeric forms—benzoid and quinoid, depending upon the nature of the solvent?

It now appeared possible to settle this question by experiment.[1] *p*-Bromotriphenylchloromethane was dissolved in benzene, ether, and toluene. The solutions were *colorless*. They were shaken with carefully dried silver chloride for days and weeks, but not the slightest change occurred. But when the same reaction was carried out in liquid *sulfur dioxide* as the solvent, then there was found to take place a complete exchange of the Br by the chlorine of the silver chloride and on evaporating the solvent *p-chloro*triphenylmethylchloride was obtained. This admits of only one interpretation:



Later, still more incontrovertible proof in favor of the quinoid character of the colored triarylmethylchlorides was obtained. The following idea suggested itself: If it be true that *p*-bromotriphenylmethylchloride in liquid sulfur dioxide is in the quinoid state (II), then the two halogen atoms must become of equal function in the molecule, both being now linked to one and the same carbon atom in the quinoid nucleus. Therefore, on the evaporation of the solvent and in the consequent restoration of the benzenoid form, the bromine will have an equal chance with the chlorine to shift to the carbinol carbon atom. The result must be the formation of some *p-chloro*triphenylmethylbromide as well as of the original *p-bromo-*

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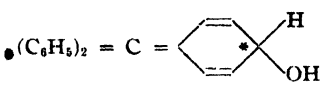
[1] *Ber.*, 40, 1860 (1907); *Ann.*, 370, 190 (1909); 376, 208 (1910).

triphenylmethylchloride, the relative amounts of the two depending upon their possible relative solubility. Experiment completely verified this presupposition.[1] Merely dissolving compound I in liquid sulfur dioxide and then allowing the latter to evaporate, induces the chlorine and bromine to exchange their relative positions.

Thus, the evidence seemed indisputable that the color formation of the sulfates and the chlorides is intimately connected with the change of the benzenoid to the quinoid form. Furthermore, since the manifestation of color and the salt-like properties of these substances are also simultaneous, the conclusion seems warranted that both of these phenomena are results of one and the same cause, *i. e.*, tautomerization to the quinoid state.[2] Consequently, these salts were named *quinocarbonium* salts, corresponding to the hypothetical *quino*carbonium base:

$(C_6H_5)_3C.OH$

Carbinol, *pseudo-base*



Quinocarbonium base

For obvious reasons the basicity was now assumed to lie in the quinone nucleus, in the C*, and not in the central carbon atom as had been originally supposed. It may also be added, that lately a number of the carbinols themselves were found capable of existing both in the quinoid state as well as in the benzoid.[3] Hence quinocarbonium bases themselves are no longer hypothetical bases.

The pursuit of this new idea, as to the function of the quinoid nucleus in imparting basicity to the molecule, was so alluring, and seemed to promise so much, that the subsequent work led us further and further away from the original problem, *i. e.*, from the immediate problem of the constitution of triphenylmethyl. It led us into the realm of the carboxonium and carbothionium salts, into that of various other oxonium salts and we found ourselves in opposition to the prevailing ideas as regards the tetravalency of oxygen in these classes of substances.

The Equilibrium Formula.

Whether our speculations respecting the valence of oxygen and the basicity of carbon be correct or not[4] may be left out of the present discussion. The significant conclusions from the results just described are these:

(1) Triphenylmethyl, *in solution*, behaves as if it had the quinol structure, either as a temporary phase or as one in equilibrium with some other phase. (2) Compounds of the type $R_3C — X$ possess the tendency to

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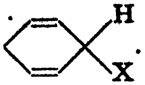
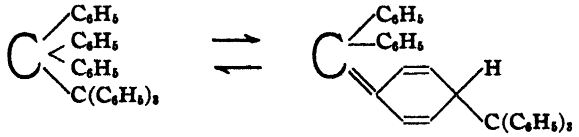
[1] *Ber.*, 42, 406 (1909).

[2] Compare Hantzsch, *Ber.*, 39, 2478 (1906).

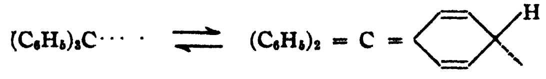
[3] THIS JOURNAL, 35, 1135 (1913).

[4] Anschütz, in the eleventh edition of *Richter's Chemistry* (1913), adopts the quinoid constitution of these salt-like compounds, as advocated in this paper.

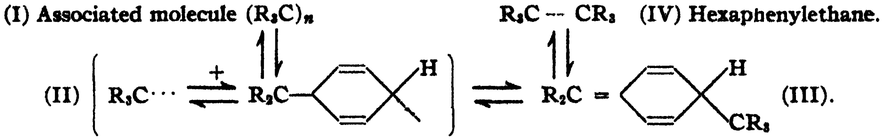
tautomerize to the quinoid modification R_2C =  (3) Since the nature of the group X may apparently vary within wide limits, then, as a corrolary to the second conclusion, it follows that hexaphenylethane, considered as a triphenylmethane derivative, may also possess the tendency toward tautomerization, and in this manner give rise to a compound of the quinol constitution:



While these new facts demanded, undoubtedly, some modifications in the simple monomolecular constitution as originally assigned to triphenylmethyl, they did not seem of such a nature as to set aside entirely the "trivalent carbon" hypothesis. Whether we assign to the dimolecular triphenylmethyl the constitution of an associated molecule, or of hexaphenylethene, or of a quinol, the chemical reactions of the unsaturated hydrocarbon are explicable only if we assume that it possesses the capacity to dissociate into free radicals. This, in my opinion, was to remain an essential part of whatever explanation might be advanced in order to account for the enigmatical behavior of this class of compounds. We need only to assume, and this assumption is perfectly consistent with the facts outlined above, that the tendency towards tautomerization is not limited to the triphenylmethane compounds alone, wherein C is tetravalent, but is also shared by the triphenylmethyl radical itself:



We then arrive at an explanation which embraces all the factors that enter into the discussion: The unsaturated character of triphenylmethyl, the existence of the two, colorless and colored, modifications, the dimolecular state in solution, the probability of the quinol-like constitution, and lastly, even the possible existence of an unstable hexaphenylethane:


(I) Associated molecule $(R_3C)_n$
R_3C — CR_3 (IV) Hexaphenylethane.
(II)
$R_3C\cdots$
+
R_2C
H
R_2C =
H
CR_3
(III).

This explanation assumes triphenylmethyl to exist in solution in various phases of constitution, all in equilibrium with each other. It accounts satisfactorily for all the facts. It becomes a matter of comparatively little consequence whether the colorless modification is assumed to be associated triphenylmethyl or hexaphenylethane. Either one would tend to give, in solution, the dimolecular triphenylmethyl of the quinol type, namely, the associated molecule through dissociation and hexaphenylethane through tautomerization. And the quinol thus produced must be in equilibrium with its products of dissociation, that is, with the two tautomeric free radicals. In other words, we can accept the quinol formulation as an intermediate phase only, and even then provided that at the same time we attribute to such a quinol the capacity to dissociate into the two free radicals.[1] It is the actual existence of these free radicals that accounts for the strange behavior of triphenylmethyl. It matters little whether the equilibrium be largely in favor of II, III, or IV, for it is a mobile, a tautomeric equilibrium. And as such it tends to restore itself as the one or the other phase is used up in a particular reaction, until the whole has reacted. Indeed, the relative equilibrium between II, III, and IV may be expected to vary with the nature of the solvent, with the temperature, and with the nature of the individual triarylmethyl under consideration.

Two Modifications of Triphenylmethyl in Solution.

Our attention should now be directed to a paper by Schmidlin,[2] in 1908, which must be considered as one of the most important contributions in this field.

The puzzling fact that the colorless triphenylmethyl gives colored solutions was first[3] attributed to possible slight oxidation. But it was soon definitely settled, in 1902, that "triphenylmethyl was white when freshly prepared. . . . .While colorless itself, the solutions of triphenylmethyl are always yellow, no matter what solvent be employed."[4] From that time on attention was repeatedly[5] called to this fact, *i. e.*, to the existence of these two modifications of triphenylmethyl, easily convertible into each other merely through changes of phase from solid to solution or *vice versa*. Schmidlin, however, observed that solutions of the colorless hydrocarbon are at first also colorless, but acquire color only after a few seconds' standing. Following up the observation, he was able to establish definitely that the colorless triphenylmethyl is only partially converted into the colored modification, that even in solution the two modifications exist side by side, in equilibrium with each other. He found that this equilibrium is greatly influenced by the nature of the solvent, by temperature, etc.,[1] and that under ordinary conditions the equilibrium is approximately one part of the colored to nine parts of the colorless modification.

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[1] Gomberg, *Ber.*, 40, 1880 (1907); 46, 228 (1913). In presenting the above "equilibrium formula" for the first time, the writer called attention to the fact that such a formulation is consistent with the facts whether we look upon the dissociation products as ions or as free radicals. The ionic interpretation became the one most widely adopted (J. Schmid, F. Henrich, Stewart, Fehling's Dictionary, etc.), although the writer himself clearly gave preference to the free-radical conception: "Die Hypothese bezüglich der Existenzfähigkeit von freiem Triphenylmethyl hat demnach den besonderen Vorteil, dass wir alle Reactionen des Kohlenwasserstoffs erklären können, ohne die Ionisationstheorie soweit ausdehnen zu müssen, das sie zu nichts anderem als zu einem leeren Spiel mit Worten wird." (*Ber.*, 40, 1884.)

[2] *Ber.*, 41, 2471 (1908).

[3] *Am. Chem. J.*, 25, 335 (1901).

[4] THIS JOURNAL, 24, 602 (1902); *Ber.*, 35, 1825 (1902).

[5] *Ber.*, 35, 2403, 2407 (1902); THIS JOURNAL, 25, 1276 (1903); *Ber.*, 36, 3929 (1903); 37, 2047 (1904); 38, 2455, 2457 (1905); 40, 1880 (1907).

Schmidlin also proved that of the two forms the colored modification is by far the more reactive. Thus, when a yellow solution of the hydrocarbon is shaken with air, the color disappears through the conversion of the colored hydrocarbon into the colorless peroxide. But in a few seconds, the yellow color of the solution reappears, due, of course, to the transformation of some more colorless into the colored modification of triphenylmethyl until the equilibrium is again restored.

These important results of Schmidlin did not, of course, invalidate in the least the theoretical conclusions in regard to the constitution of triphenylmethyl that have been set forth in the preceding pages, for these conclusions invariably took into consideration the existence of two modifications of triphenylmethyl. But Schmidlin's results did emphasize in the most striking manner that the relation of these two modifications to each other is even more intimate than had been previously supposed, and they also served to emphasize again that no constitution of triphenylmethyl could be considered satisfactory which did not account for the ready transformation of the two modifications into each other.

Tentative explanations in regard to the relation between the two modifications of triphenylmethyl were not lacking. In 1902[2] it was ascribed to the ionization of the hydrocarbon in solution into two oppositely charged ions, R_3C^+, R_3C^-. In 1905, a simple suggestion was made by Flürscheim,[3] namely, that the colorless hexaphenylethane dissociates in solution into colored free radicals, triphenylmethyl. In 1906,[4] for the first time, positive experimental evidence was obtained that the change of the colorless into the colored form is accompanied by the production of some kind of a quinoid constitution. In the same year, a little later, but independently, Chichibabin[5] suggests the possible existence of tautomerism between hexaphenylethane and some kind of colored quinol, according to Heintschel or to Jacobson; but on the next page, in the same paper, he cites evidence which, he thinks, "spricht gegen die quinoiden Structur-

[1] It varies also with concentration of solution (Piccard, *Ann.*, 381, 347 (1911)).

[2] Gomberg, *Ber.*, 35, 2403 (1902); 40, 1882 (1907).

[3] *J. prakt. Chem.*, 71, 505 (1905).

[4] Gomberg, *Ber.*, 39, 3297 (1906).

[5] *J. prakt. Chem.*, 74, 342 (1906).

formeln des Triphenylmethyls," an opinion which he most strongly upholds in his next paper.[1] In 1907, based upon evidence from extensive experiments, the "equilibrium formula" was suggested, *i. e.*, associated molecule (or hexaphenylethane) ⟶ quinol ⟶ free tautomeric radicals; the production of color being due either to the dimolecular quinol or to the *quinoid* monomolecular radical.

The "equilibrium formula" is in full harmony with the facts known up to the present, but the explanation—hexaphenylethane ⟶ triphenylmethyl, is finding a wider acceptance, largely because of its simplicity.

We have now reached the end of the second period of the hypothesis relative to the existence of free radicals. During this period the trivalency hypothesis still had its adherents. Werner (1906), Schmidlin (1908), Wieland (1909), and many others spoke in favor of it. And yet, on the whole, the majority of chemists, I think, came to look upon triphenylmethyl either as unstable hexaphenylethane, or as a quinol, some admitting probable partial dissociation into radicals or ions, others refusing to admit it. Anschütz, in the tenth edition of Richter's Organic Chemistry (1905), gives equal weight to the two interpretations, the free radical and hexaphenylethane. W. A. Noyes, in the German edition of his Organic Text (1907) speaks of it as hexaphenylethane. Nernst, in the fifth edition of the Theoretical Chemistry (1907), leaves out the mention of the trivalency of carbon which was recorded in the preceding edition. Henrich, in the first edition of his "*Anschauungen über organische Chemie*" (1908), gives preference to the equilibrium idea. So does Stewart in his "Recent Advances in Organic Chemistry" (1910). Holleman-Walker, in the third English edition (1910), are undecided between triphenylmethyl and hexaphenylethane. Jacobson and Stelzner, in the second edition of Meyer and Jacobson's *Lehrbuch*, speak of triphenylmethyl in the early part of the first volume (p. 65, written in 1905), as a free radical, but in the latter part of the first volume (p. 788, written in 1907), as a substance of double the molecular weight, with probable dissociation into parts. Many other similarly divergent views could be cited.

VIII. Constitution, Third Period (1910–).

Monomolecular Triarylmethyls.—As the hexaphenylethane and the quinol constitution were gaining ascendency over the simple triphenylmethyl idea, and all because of the double molecular weight, and as the actual reality of free radicals was appearing to many more and more dubious, a paper by Schlenk,[2] 1910, gave a new turn to the subject.

In studying analogs of triphenylmethyl, he prepared the following compounds:

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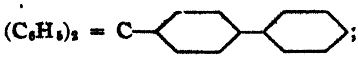
[1] *Ber.*, 40, 3970 (1907).

[2] Schlenk, Weickel u. Herzenstein, *Ann.*, 372, 1 (1910); *Ber.*, 43, 1754 (1910).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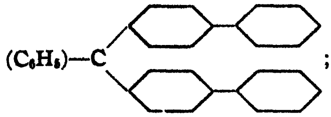
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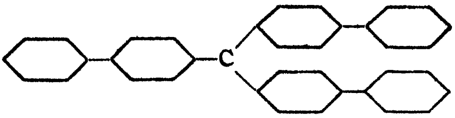

He found that these analogs resemble triphenylmethyl itself in every characteristic. They are colored, the intensity increasing with the number of *bi*-phenyl groups; they are unstable, readily absorb oxygen from the air and form peroxides, etc. But when the molecular weight of these unsaturated triarylmethyls was determined he found, unexpectedly, that some of these hydrocarbons exist largely as monomolecular. To be more specific: The tri-*bi*-phenylmethyl was found to be entirely monomolecular; the di-*bi*-phenyl, to the extent of 80% monomolecular; and the mono-*bi*-phenyl only to the extent of 15%.

There can be but one inference—these compounds exist as free radicals. And as the characteristic reactions of these bodies are entirely similar to those of triphenylmethyl itself, the reactions of the latter must also be due to the presence of more or less of the actual, free, triphenylmethyl radical, whatever its immediate predecessor. The supposed existence of free radicals, with carbon trivalent, becomes therefore indisputable.

With the recognition of the highly important fact that some triarylmethyls exist as wholly monomolecular the only serious obstacle and argument against the hypothesis of free radicals vanished. Soon after that, many other analogs of triphenylmethyl were found to be monomolecular.[1]

Attention was now again directed to the molecular weight of triphenylmethyl itself. The molecular-weight determinations that have been made in 1904[2] indicated that at least in naphthalene monomolecular triphenylmethyl may be assumed to exist as such. Wieland[3] now computed that the amounts of the monomolecular hydrocarbon, as calculated from these molecular-weight determinations—17% in naphthalene, 5% in benzene—are of the same order of magnitude as the equilibrium ratio between the colorless and the yellow modification in solvents as found by Schmidlin. From this he draws the inference that the yellow modification is in reality monomolecular triphenylmethyl. Later, Piccard,[4] Schmidlin,[5] and also Schlenk and Mair,[6] employing diverse methods, arrived at the conclusion that *all* solutions of triphenylmethyl contain actually monomolecular triphenylmethyl, the amount of this in benzene at 80° reaching 25-30% of the whole amount of the hydrocarbon dissolved.

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[1] Schlenk and Rennig, *Ann.*, **394**, 180 (1912); Chichibabin and Korjagin, *J. prakt. Chem.*, **88**, 516 (1913).

[2] Gomberg and Cone, *Ber.*, **37**, 2037 (1904).

[3] *Ber.*, **42**, 3029 (1909).

[4] *Ann.*, **381**, 347 (1911).

[5] *Ber.*, **45**, 3180 (1912).

[6] *Ann.*, **394**, 179 (1912).

Some Unsettled Questions.—But while the existence of free radicals, with carbon as trivalent, is thus firmly established, some of the minor features of this subject are not as yet as completely cleared up as one might judge from the current literature.

It has become customary to speak of the *colorless* triphenylmethyl as hexaphenylethane, in distinction to the colored modification as the actual free radical. But how vastly different is this modern conception of hexaphenylethane from the older idea! The *new* hexaphenylethane is an altogether different substance from what has been implied by that term before. Unstable it still is, and is indeed very easily broken down by a variety of reagents, but more than that: even if no extraneous force be present to break it up, the hydrocarbon still decomposes spontaneously in virtue of its inherent tendency to dissociate into two halves. And so we come in the case of hexaphenylethane to the same fundamental idea which the writer applied to the quinol formula. The quinol constitution, too, seemed acceptable as an intermediate phase only on the condition that the hydrocarbon be considered as possessing the capacity to dissociate spontaneously into two dissimilar free radicals. We mean real, actual dissociation, where the products are not of a fleeting temporary nature, but where they are entities and have a lasting existence. It is indeed far more probable, as we have expressed it in the equilibrium formula, that both the hexaphenylethane and the quinol formulae are but two tautomeric modifications of one and the same constitution, and that in solutions of the hydrocarbon, both exist side by side in equilibrium with each other. The results of the experiments described in the earlier part of this paper, the facility with which *p*-halogen in triarylmethyls can be removed must, in some way, be accounted for. The hexaphenylethane constitution does not explain them; but hexaphenylethane tautomerized accounts for those results completely, as completely as does a physically associated dimolecular molecule.

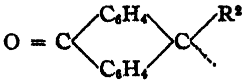
There is still another uncertainty which requires further study. It is now definitely established that the colored modification of triarylmethyls is monomolecular, and this applies even to those in the solid state, as for instance, to tri-*bi*-phenylmethyl. There is no better way at present at hand to explain this than by attributing to triphenylmethyl itself, as is done in the equilibrium formula, the capacity to undergo the same kind of tautomerization to the quinoid state as so many of its derivatives undergo. To say, as is being done, that hexaphenylethane is colorless and a radical with carbon in the trivalent state is colored, is to assert something for which at present there is no anology. Such a statement is not an explanation. It is an assertion which may be right, or wrong.

But after all, these are minor points. The really important issue—the existence of free radicals, the trivalency of carbon—that has been established.

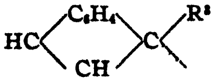
IX. Analogs of Triphenylmethyl.

As has been mentioned in the introduction, triphenylmethyl is but an example, the simplest and most completely investigated example, of the class of the triarylmethyls. No systematic study of any particular subgroup of such free radicals has as yet been made or undertaken. The existence of about thirty-five free radicals has been demonstrated in our laboratory and as many more in other laboratories, and there is no reason to doubt that this new class of compounds will, in time, become fully as extensive as the classes of alcohols, ketones, acids, etc. Such instances of free radicals as are at present known, have been prepared with the idea to elucidate some definite feature of theoretical interest. It is now well established that the three aromatic groups around the central carbon atom may vary to any extent—some may be nitro-phenyl groups, or hydroxy-, methoxy-, bromo-, carboxy-phenyl, or they may be naphthyl groups. Also, as has been recently shown in our laboratory,[1] one of the three aromatic groups may be replaced by a non aromatic thienyl group, C_4H_3S. Furthermore, free radicals with a trivalent carbon atom have been obtained from compounds which belong to the following well-known series:

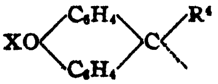
Anthracene series.........................



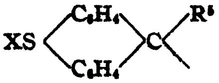
Indene series,.........................



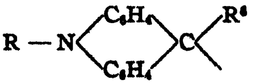
Xanthone series.........................



Thioxanthone series.........................



Acridine series.........................



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[1] Gomberg and Jickling, THIS JOURNAL, 35, 446 (1913).

[2] Liebermann, *Ber.*, 37, 3340 (1904).

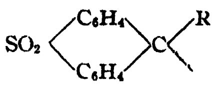
[3] Kohler, *Am. Chem. J.*, 40, 217 (1908).

[4] Gomberg and Cone, *Ann.*, 370, 142 (1909); Gomberg and West, THIS JOURNAL, 34, 1529 (1912).

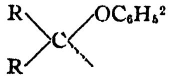
[5] Gomberg and Cone, *Ann.*, 376, 183 (1910).

[6] Cone, THIS JOURNAL, 34, 1703 (1912); and results to be published soon.

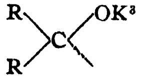
Benzophenone sulphone series . . . .



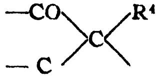
Diaryl-phenoxymethyl . . . . .



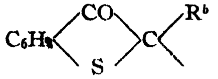
Aromatic ketones . . . .



Naphthalene series containing the group . . . . .



Thio-indigo series . . . .



X. Historical.

Gay Lussac, in 1815, began his important studies upon cyanogen derivatives. He obtained cyanogen itself from mercuric cyanide and defined it as "a compound radical," functioning in its derivatives in the same manner as the elements, or "simple radicals," do in their derivatives, respectfully. According to Gay Lussac's idea cyanogen (CN), was a *free* radical. Dumas and Boullay later, in 1828, extended this fundamental notion of the existence of free radicals to organic compounds. They set up the theory that "etherin," —C_2H_4— , is the "compound radical" from which alcohol, ether, chloroethane, etc., are derived. In support of their contention they pointed to the existence of this radical in the free state, the gas ethylene. Liebig and Wöhler, 1832, published their memorable paper upon the "benzoyl radical." They defined a radical very much as we do now, "a never varying constituent of a series of compounds." Liebig did not oppose the idea concerning the existence of free radicals. On the contrary, he even predicted the possible isolation of alcohol radicals, which might be effected by the action of potassium on the iodides of such radicals. Berzelius and Dumas joined Liebig for a time, and their efforts were turned to discovering new radicals. Organic chemistry came to be defined as the chemistry of compound radicals. Much support was added to this view by the remarkable work of Bunsen. Between 1839 and 1843 he prepared various derivatives of "cacodyl," the chloride, the oxide, etc., and also the cacodyl itself, which he considered as a free radical, $As(C_2H_6)$, and to which was later given the more specific constitution $As(CH_3)_2$. Then followed the important work of

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[1] From results to be published soon.

[2] Wieland, *Ber.*, 44, 2550 (1911).

[3] Schlenk and Weickel, *Ber.*, 44, 1182 (1911); 46, 2840 (1913).

[4] Pummerer, *Z. angew. Chem.*, 26, 549 (1913).

[5] Kalb and Bayer, *Ber.*, 46, 3881 (1913).

Frankland, and of Kolbe, 1849–1850. The former claimed to have isolated the radicals—*methyl*, *ethyl*, *etc.*—by the action of zinc upon the corresponding iodides, while Kolbe obtained the same radicals by the hydrolysis of the sodium salts of acetic, propionic and such acids. In vain did Gerhard and Laurent insist that the molecular formulas of all these so-called free radicals must be doubled, in accordance with Avogadro's hypothesis. The existence of free radicals was generally accepted as late as 1865, fifty years after Gay Lussac's introduction of this idea into chemistry. Even Kekulé for a time considered Frankland's "methyl" as distinct from ethane. But in 1864 Schorlemmer showed by experimental evidence that Frankland's and Kolbe's methyl and ethyl were nothing else than ethane and butane. From that time on, the question relative to the existence of free radicals was never seriously raised until the discovery of triphenylmethyl.

How parallel these two periods in the history of chemistry are! Now, as then, a methyl was prepared by the abstraction of halogen from the corresponding alkyl-halide. Now, as then, it was found that the molecular weight of the product must be doubled. But now, unlike as in the period of fifty years ago, it was possible to show, by physical and chemical evidence, that the product which results from the coupling of the radicals is at best unstable. It was possible to show that it does not retain its individuality, but tends to break down again and is in equilibrium with the truly free radicals. And so we find ourselves obliged to reintroduce the conception of free radicals, and also to introduce the supplementary notion of organic substances existing under certain conditions in a state of actual dissociation.

What the future holds in regard to this new revival of the much disputed question is difficult to foretell. As a working hypothesis it has fully justified its existence, it has opened a new branch of organic chemistry.

ANN ARBOR, MICH.

SYNTHESIS OF DEPSIDES, LICHEN-SUBSTANCES AND TANNINS.

BY EMIL FISCHER.[1]

Received April 30, 1914.

Gentlemen:

The substances mentioned in the title are ester-like derivatives of the phenol carbonic acids, to which belongs gallic acid, so widely distributed in the plant kingdom and discovered in 1786 by C. W. Scheele, as well as the famous remedy salicylic acid, and which, therefore, are interesting, not alone to chemists, but also to the plant physiologists and the medical profession. Their study occupies a large space in the history of the aromatic group, and it gives me pleasure to refer to the fact that, at no place, so much has been worked out concerning these substances as right here in Vienna. It suffices to recall the investigations of F. Rochleder, H. Hlasiwetz, L. Barth and recently of J. Herzig and his students.

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[1] Address delivered before the Naturforscher-Versammlung, Vienna, Sept. 23, 1913; and published in *Ber.*, 46, 3253–89 (1913). Translated by Frank Rose Elder, Columbia University, and published here through the courtesy and with the consent of Excellent Fischer and of the editors of the *Berichte*.

These phenol carbonic acids possess, among other properties, the ability to form ester-like anhydrides with one another, in such a manner that the carboxyl of the first molecule unites with the phenol group of the second. As the simplest example, I would cite the first anhydride of hydroxybenzoic acid:

$$HO.C_6H_4.CO.O.C_6H_4.COOH$$

By similar coupling of a third molecule of hydroxybenzoic acid the following system results:

$$HO.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.COOH$$

Such ester-like anhydrides, Freudenberg and I have named[1] "depsides." The word is derived from the Greek δε'ψειν (to tan), because many of these substances show resemblances to the tannins. According to the number of phenol carbonic acids which are coupled together, one distinguishes didepsides, tridepsides, tetradepsides. Thus the nomenclature is formulated as in the case of the polysaccharides and polypeptides. Such depsides are nowise new, for the two substances just mentioned above, the di- and tridepsides of *p*-hydroxybenzoic acid, were obtained by Klepl in 1883[2] by simply heating *p*-hydroxybenzoic acid. But his simple procedure is not applicable to most of the other phenol carbonic acids, as they cannot stand the necessarily high temperature. Still older are the exhaustive investigations of Schiff,[3] on the formation of similar substances from the phenol carbonic acids by dehydrating agents.

By treatment of gallic acid with phosphorus oxychloride, Ch. Gerhardt,[4] in 1853, prepared the amorphous anhydride of salicylic acid from sodium salicylate, obtaining an amorphous product which showed the tannin reactions, and which he considered to be digallic acid, $C_{14}H_{10}O_9$. Prior to this, J. Löwe[5] had observed that gallic acid, when heated with arsenic acid, was changed into a tannin-like body. On repetition of the experiment, Schiff came to the conclusion that this product was also digallic acid. Later he and his students applied the anhydrization by phosphorus oxychloride to a whole series of other phenol carbonic acids, protocatechuic acid, salicylic acid, *m*-hydroxybenzoic acid, cresotinic acid, phloretic acid and pyrogallol carbonic acid. According to the conditions, didepsides or complicated anhydrides resulted.

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[1] *Ann.*, **372**, 35 (1910).

[2] *J. prakt. Chem.*, [2] **28**, 208.

[3] *Ber.*, **4**, 232, 967 (1871); *Ann.*, **170**, 43 (1873); **163**, 218, 219 (1872); **172**, 356 (1874); *Ber.*, **15**, 2588 (1882); *Gazz. chim. ital.*, **17**, 552 (1887); *Ann.*, **252**, 87 (1889).

[4] *Ann.*, **87**, 159.

[5] *J.*, **1868**, 559.

Unfortunately, the majority of depsides described by Schiff are amorphous, and, therefore, have not withstood criticism concerning their individuality and composition. In particular, his view that the amorphous digallic acid is identical with tannin cannot be maintained.[1] This will be returned to later.

However, the procedure of Schiff, repeated in other hands, has led to sharply defined didepsides. Thus, in a patent of the firm of C. F. Böhringer and Son[2] is cited a useful process for preparing disalicylic acid with phosphorus oxychloride and I, together with Freudenberg, have shown that by the same treatment of *p*-hydroxybenzoic acid, under certain conditions, the didepside of the acid discovered by Klepl[3] is obtained in excellent yield.

Besides the depsides, which are true acids, the phenol carbonic acids also may form neutral anhydrides. To this class belongs the *p*-hydroxybenzoide $(C_7H_4O_2)_x$, of Klepl; then the different salicylides, cresotides, phloretides and probably also the tetra-*p*-hydroxybenzoide[4] of Schiff. These, however, cannot be further considered here.

The inducement to take up the synthesis of the depsides was presented by the following observation in the synthesis of polypeptides of tyrosine: For the preparation of glycyltyrosylglycine, a chloride of chloroacetyl tyrosine was necessary. Since the free phenol group appears to hinder the action of phosphorus chloride, I thought of the scheme of protecting the latter by introducing a group which subsequently could be easily removed, and chose for this purpose the carbomethoxy group.[5] The application of this process to the common phenol carbonic acids is the starting point for all the products which I will take up today. I have, in this investigation, enjoyed the valuable assistance of different young professional colleagues, whose share is evident from the titles of the single publications, and of these I will mention particularly Mr. Karl Freudenberg.

Carbomethoxylation of the Phenolcarbonic Acids.

Carboalkoxy derivatives of the common phenols have been long known. However, with a single exception,[6] which I will later mention particularly, these derivatives of their carbonic acids were lacking. It is now known that such substances result easily by the action of chlorocarbonic alkyl ester and alkali on phenol carbonic acids in cold aqueous solution.[1]

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[1] Freda, *Gazz. chim. ital.*, **8**, 9, 363 (1878); **9**, 327 (1879); Bignelli, *Chem. Zentr.*, **1909**, II, 1861–3; **1910**, II, 23; cf. further the later history of the tannins.

[2] D. R. P., 211,403; cf. *Chem. Zentr.*, **1909**, II, 319, 1285.

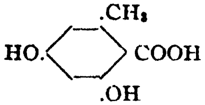
[3] *Ann.*, **372**, 45 (1910).

[4] *Ber.*, **15**, 2588 (1882).

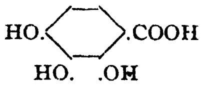
[5] *Ibid.*, **41**, 2860 (1908).

[6] Carboethoxy-salicylic acid of F. Hofmann.

The course of the reaction is particularly smooth, if the phenol group is in the *meta* or *para* position to the carboxyl and, the accumulation of hydroxyl groups is no obstacle; for protocatechuic acid and gallic acid can be completely carbomethoxylated with slightly more than the theoretical quantity of chlorocarbonic methyl ester. The behavior is somewhat otherwise if a hydroxyl stands next to a carboxyl. Sometimes the complete carbomethoxylation succeeds in aqueous alkaline solution with an excess of chlorocarbonic methyl ester, as the case of orsellinic acid[2] and pyrogallolcarbonic acid,[3] demonstrates.

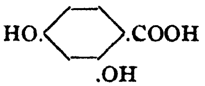


Orsellinic acid



Pyrogallolcarbonic acid.

In other cases, under the same conditions, the ortho hydroxyl remains incompletely carbomethoxylated, even if a large excess of the reagent is employed. The case of β-resorcylic acid has been more minutely investigated.[4]



Salicylic acid behaves similarly. The complete carbomethoxylation of this latter acid can be attained by treatment with chlorocarbonic methyl ester in presence of dimethyl aniline in an indifferent solvent, for example, benzene. The process was first used by Fritz Hofmann for the preparation of carboethoxy salicylic acid, but has only been described in an American patent (No. 1,639,174 of Dec. 12, 1899), which has been recorded neither in the scientific nor in the collected chemical patent literature. I learned of it only by chance, in a private communication from Mr. A. Einhorn, just at a time when I was occupied in working out such a method myself. We have since applied the process with success, not alone to salicylic acid,[5] but also to some other *o*-phenolcarbonic acids, such as the just mentioned β-resorcylic acid,[6] and the isomeric gentisic acid[7] (hydroquinone carbonic acid). Even with phloroglucine carbonic acid,[8] which in aqueous alkaline solution takes on only one carbomethoxy group, the process succeeds if one uses a large excess of chlorocarbonic methyl ester and dimethyl aniline. However, the carboxyl group is also affected,* and it forms an indifferent product, probably of anhydride-like nature. This, however, can be destroyed (as I, in conjunction with H. Strauss, have shown), by bicarbonate in acetone solution, without splitting off the carbomethoxy group. By this artifice, which is also applicable in other cases, the preparation of tricarbomethoxy phloroglucine carbonic acid,[1] succeeded without difficulty and thus it appears that the method is sufficiently complete to be available for all phenol carbonic acids.

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[1] E. Fischer, *Ber.*, 41, 2875 (1908).

[2] E. Fischer and K. Hoesch, *Ann.*, 391, 366 (1912).

[3] E. Fischer and M. Rapaport, *Ber.*, 46, 2389 (1913).

[4] E. Fischer and K. Freudenberg, *Ann.*, 384, 234 (1911).

[5] *Ber.*, 42, 218 (1909).

[6] *Ibid.*, 42, 225 (1909).

[7] *Ibid.*, 42, 223 (1909).

[8] *Ann.*, 371, 306 (1910).

It is remarkable that the difficulty encountered with the *ortho* phenol group disappears, if the carboxyl is not directly attached to the benzene nucleus; for *o*-coumaric acid (*o*-hydroxy cinnamic acid) can be very easily carbomethoxylated in aqueous alkaline solution. So far, the following acids have been completely carbomethoxylated:

(*a*) In aqueous alkaline solution:
  p-Hydroxybenzoic acid (*Ber.*, **41**, 2877 (1908))
  m-Hydroxybenzoic acid (will be published later)
  Vanillic acid (*Ann.*, **372**, 47 (1910))
  o-Coumaric acid (*Ber.*, **42**, 226 (1909))
  Phloretic acid (will be published later)
  Caffeic acid (will be published later)
  Ferulic acid (*Ann.*, **391**, 357 (1912))
  Protocatechuic acid (*Ber.*, **41**, 2881 (1908))
  α-Resorcylic acid (*Ber.*, **46**, 1145 (1913))
  Orsellinic acid (*Ann.*, **391**, 366 (1912))
  Gallic acid (*Ber.*, **41**, 2882 (1908))
  Pyrogallolcarbonic acid (*Ber.*, **46**, 2390 (1913))
  Syringic acid (will be published later)

(*b*) According to the process of F. Hofmann:
  Salicylic acid (*Ber.*, **42**, 218 (1909))
  α- and β-Hydroxynaphthoic acids (*Ann.*, **391**, 352, 355 (1912))
  β-Resorcylic acid (*Ber.*, **42**, 225 (1909))
  Gentisic acid (*Ber.*, **42**, 223 (1909))
  Phloroglucinecarbonic acid (*Ber.*, **46**, 2400 (1913))

With the polyphenol carbonic acids, there is naturally the possibility of partial carbomethoxylation. They are governed by the orienting influence which the carboxyl exercises on the entrance of the carbomethoxy group. On this point the following data have, so far, been gathered: In the *o*-, *p*-dihydroxybenzoic acid, the carbomethoxy group enters preferably in the *p*-position; and, if one decreases the quantity of chlorocarbonic ester to one mol, with gentisic acid,[2] β-resorcylic acid and orsellinic acid,[3] the *p*-monocarbomethoxy compound can be isolated in moderately pure condition.

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[1] E. Fischer and H. Strauss, *Ber.*, **46**, 2400 (1913).

[2] *Ber.*, **42**, 222, 224 (1909).

[3] E. Fischer and K. Hoesch, *Ann.*, **391**, 364 (1912).

It is otherwise with gallic acid; for here the first carbomethoxy group enters preferably in the *m*-position,[1] perhaps because the *p*-hydroxyl is protected from reaction by the two other neighboring hydroxyls. Partial carbomethoxylation succeeds easily with phloroglucinecarbonic acid; for in aqueous alkaline solution it takes on only one carbomethoxy group, and that happens most probably in the para position.[2]

The change from carbomethoxy compounds back to phenolcarbonic acids is accomplished with extraordinary ease by excess of cold aqueous alkali. Aqueous N ammonia acts similarly, though somewhat more slowly; but the carbomethoxy group is then split off mostly as urethane and not as carbonate. Neutral alkali carbonate also acts in the cold, but more slowly; while bicarbonate is rather indifferent, and thus, in most cases, serves to dissolve the acids. Only a few difficultly soluble alkali salts were encountered.

By insufficient quantity of alkali, partial elimination of the carbomethoxy groups results. Thus there was obtained from the dicarbomethoxyprotocatechuic acid, the *m*-monocarbomethoxy compound;[3] and from the tricarbomethoxygallic acid, the 3,5-dicarbomethoxy compound.[4] In both cases, preferably the *p*-carbomethoxy group was split off.

These partially carbomethoxylated substances have played a role in the synthesis of didepsides which will be spoken of later.

Furthermore, they can be methylated by diazomethane, whereby the carboxyl is esterified and all the free phenol groups methylated. These esters then yield, by double saponification, the corresponding partially methylated phenolcarbonic acids. In such a way, the structure of the monocarbomethoxyprotocatechuic acid,[5] and of the 3,5-dicarbomethoxygallic acid,[6] was determined.

The same process is also adapted to the practical preparation of such partially methylated substances as are difficult to prepare in other ways. In this manner, the *o*-methyl ethers of gentisic acid,[7] β-resorcylic acid[7] and orsellinic acid[8] were prepared; as well as the *o,o*-dimethyl ether of phloroglucinecarbonic acid,[7] the *p*-methyl ether[7] and the *m,p*-dimethyl ether of gallic acid.[9]

It is worth noticing that with the above-mentioned esters of carbomethoxylated phenolcarbonic acids, the ester group is removed more easily by cold concentrated sulfuric acid, the carbomethoxy group on the other hand more easily by cold alkali.

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[1] E. Fischer and K. Freudenberg, *Ber.*, **45**, 2716 (1912).

[2] *Ann.*, **371**, 306 (1910).

[3] E. Fischer and K. Freudenberg, *Ibid.*, **384**, 235 (1911).

[4] E. Fischer, *Ber.*, **41**, 2885 (1908); further, E. Fischer and K Freudenberg, *Ann.*, **384**, 240 (1911); cf. E. Fischer and O. Pfeffer, *Ibid*, **389**, 211–4 (1912).

[5] E. Fischer and K. Freudenberg, *Ibid.*, **384**, 236 (1911).

[6] E. Fischer and O. Pfeffer, *Ibid.*, **389**, 199 (1912).

[7] *Ibid.*, **389**, 199 ff. (1912).

[8] E. Fischer and K. Hoesch, *Ibid.*, **391**, 372 (1912).

[9] E. Fischer and K. Freudenberg, *Ber.*, **45**, 2717 (1912).

Chlorides of the Carbomethoxyphenolcarbonic Acids.

These result from the action of phosphorus pentachloride on the acids, are usually crystalline, and show the important reactions of benzoyl chloride. Since, further, the carbomethoxy group can be subsequently easily removed, they have been valuable materials for synthesis.

It would naturally be still simpler to use in their place the chlorides of the phenolcarbonic acids themselves, but their preparation involves difficulties. In the action of phosphorus pentachloride it is well known that, besides the carboxyl, the phenol group is attacked, as R. Anschütz has shown in many cases. Only when the hydroxyl is crowded in between a neighboring carboxyl and a second *o*-substituent, is it removed from the action of phosphorus chloride and thus permits the preparation of the simple acid chloride.[1]

The chlorides of the phenolcarbonic acids can, as a rule, be prepared, directly according to the method of H. Meyer,[2] by heating with thionyl chloride; but the products are with few exceptions oils, whose individuality appears doubtful to me, and from which the discoverer, aside from the esters, has prepared no other derivatives of the phenolcarbonic acids. Thus they cannot be compared in regard to usefulness, with the well behaved and relatively stable chlorides of the carbomethoxy phenolcarbonic acids. The process of Meyer has recently been improved by Kopetschni and Karzag, in that, in the place of the free acid, the alkali salt is treated with thionyl chloride. In this way they succeeded in obtaining a crystalline salicylic acid chloride.[3]

Finally, the chlorides of the completely methylated or acetylated phenolcarbonic acids have been long known. They are sufficiently stable to be of service in synthesis. But, the later removal of the methyl or acetyl group demands energetic treatment with acids or alkalies, and is thus excluded for all products which, by this treatment, undergo further change, for example, with the ester-like derivatives of the phenolcarbonic acids.

The chlorides of all the above-mentioned carbomethoxylated phenolcarbonic acids have been prepared by use of phosphorus pentachloride, either by gentle heating, or, in the case of sensitive substances, by shaking the acid and pentachloride with dry chloroform. If the chloride crystallizes with difficulty, it is advisable to remove the phosphorus oxychloride by dilution of the chloroform solution and by long, very gentle, heating of the residue in a high vacuum.

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[1] Anschütz, *Ber.*, 30, 221 (1897).

[2] *Monatsh.*, 22, 415 (1901).

[3] *Chem. Zentr.*, 1913, II, 728.

Most of the chlorides were obtained crystalline, only the tricarbomethoxy phloroglucinecarbonic acid, carbomethoxysalicylic acid, and carbomethoxyphloretic acid have so far remained as oils. The last two, however, can be sufficiently purified by distillation in a high vacuum.

These chlorides have been used, so far, for the following syntheses:

1. With alcohols they immediately form esters, which, by subsequent saponification with alkali, are changed into the ester of the free phenolcarbonic acid. An example is the preparation of ethyl gallate.[1] The method, naturally, has here no practical significance, because the esterification of the phenolcarbonic acids with the monohydric alcohols is attained much more conveniently by older methods. On the other hand the process acquires great importance in its application to the polyhydric alcohols and especially in the sugar series. This will be fully considered later.

2. The chlorides act energetically on the esters of amino acids and can be coupled with amino acids in aqueous alkaline solution. By subsequent splitting off of the carbomethoxy group there results finally the derivative of the phenolcarbonic acid. As an example, the synthesis of *p*-hydroxyhippuric acid (*p*-hydroxybenzuric acid)[2] may serve. It is accomplished according to the following equations:

$$CH_3CO_2.O.C_6H_4.CO.Cl + 2NH_2.CH_2.CO_2C_2H_5 =$$
$$CH_3CO_2.OC_6H_4.CO.NH.CH_2.CO_2C_2H_5 + HCl.NH_2.CH_2.CO_2C_2H_5$$

$$CH_3CO_2.O.C_6H_4.CO.NH.CH_2CO_2C_2H_5 + 3NaOH =$$
$$HO.C_6H_4.CO.NH.CH_2COONa + Na_2CO_3 + C_2H_6O + CH_4O$$

Similarly, the isomeric salicyluric acid was prepared.[3] The process appears, to me, to be much better than the one used somewhat earlier by Bondi[4] for the preparation of salicyluric acid from glycocoll and salicylic acid azide. Finally, there is still to be mentioned the synthesis of 3,4-dihydroxyhippuric acid from the chloride of the dicarbomethoxyprotocatechuic acid and glycocoll ester,[5] as well as of vanilloylglycine from the chloride of carbomethoxyvanillic acid.[6] I do not doubt that this method is sufficient for the preparation of numerous combinations of this sort.

3. Under the influence of aluminium chloride, the chlorides unite easily with benzene, and on subsequent splitting off of the carbomethoxy group, there results the unsymmetrical hydroxy derivatives of benzophenone. For *p*-hydroxybenzophenone,[7] the synthesis runs according to the following equations:

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[1] *Ber.*, 42, 1022 (1909).

[2] *Ibid.*, 41, 2880 (1908).

[3] *Ibid.*, 42, 219 (1909).

[4] *Z. physiol. chem.*, 52, 170 (1907).

[5] T. Kametaka, *Ber.*, 42, 1482 (1909).

[6] E. Fischer and K. Freudenberg, *Ann.*, 372, 66 (1910).

[7] *Ber.*, 42, 1017 (1909).

$$CH_3CO_2.O.C_6H_4.CO.Cl + C_6H_6 = CH_3CO_2.O.C_6H_4.CO.C_6H_5 + HCl$$

$$CH_3CO_2.O.C_6H_4.CO.C_6H_5 + 3NaOH = Na_2CO_3 + CH_3OH + H_2O + NaO.C_6H_4.CO.C_6H_5.$$

In this manner, there was prepared from α-resorcylic acid the 3,5-dihydroxybenzophenone,[1] from gallic acid the 3,4,5-trihydroxybenzophenone,[2] and from β-resorcylic acid the already known 2,4-dihydroxybenzophenone.[3] Finally, pyrogallolcarbonic acid gave the isomeric, 2,3,4-trihydroxybenzophenone,[4] which is identical with the mordant dyestuff known under the name of alizarin yellow A, and thus its structure is established beyond doubt.

4. The chlorides can be coupled with the free phenolcarbonic acids and, by subsequent splitting off of the carbomethoxy group, didepsides obtained. By repetition of the operation, tri- and tetradepsides were prepared. The process is susceptible of many variations, as the following sections will show.

The applicability of the chlorides for synthesis is certainly not exhausted by these reactions. One can hope that they will be useful in most cases where benzoyl chloride and its derivatives have already proven themselves of service, and where it is desired to regain the phenol group by very mild hydrolysis. Thus, I believe without hesitation, that the chloride of carbomethoxy ferulic acid can be recommended for the experiment on the building up of curcumin, just as V. Lampe and J. Milobedzka[5] have succeeded in preparing the similar dicinnamoylmethane.

Didepsides.

Their history has been so adequately treated before that I must here content myself by describing only the new method. *p*-Hydroxybenzoic acid serves for the simplest case of the synthesis. The chloride of its carbomethoxy derivative unites with *p*-hydroxybenzoic acid in cold, aqueous alkaline solution, according to the following equations, and there results the alkali salt of carbomethoxy-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid:[6]

$$CH_3CO_2.O.C_6H_4.CO.Cl + NaO.C_6H_4.COONa = NaCl + CH_3CO_2.O.C_6H_4.CO.O.C_6H_4.CO_2Na$$

On account of its slight solubility, it separates from its aqueous solution as the crystalline salt, but can be easily changed to the free acid by cold hydrochloric acid. In most other cases, the alkali salts are easily soluble in water and the resulting aqueous liquid is precipitated directly by mineral acid.

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[1] E. Fischer and H. O. L. Fischer, *Ber.*, 46, 1147 (1913).

[2] *Ibid.*, 42, 1018 (1909).

[3] *Ann.*, 371, 317 (1910).

[4] E. Fischer and M. Rapaport, *Ber.*, 46, 2393 (1913).

[5] *Ber.*, 46, 2235 (1913).

[6] *Ibid.*, 42, 216 (1909).

Since the chlorides used are ordinarily solid and in this form react too slowly, I, at first, used ethereal solutions for this coupling; later, acetone solution[1] was shown to be preferable in the majority of cases, and many couplings can be carried out satisfactorily only by use of this expedient. The ordinary procedure is as follows: The phenolcarbonic acid to be coupled is dissolved in the calculated quantity of N or $2\ N$ alkali, some acetone added, the whole cooled to a low temperature and to this solution is added, in several alternate portions, another 1.1 mol of $2\ N$ alkali and a solution of the chloride in dry acetone, the mixture being well stirred. The coupling takes place very quickly and completely even at low temperature. In most cases, the difficultly soluble coupled product can be precipitated by acidification and dilution with water. In other cases, the acetone is distilled off at low pressure, or the liquid is extracted with ether directly after acidification and dilution.

Instead of the alkali, dimethyl aniline can be used as the base, and the coupling can be carried out with exclusion of water. An example of this sort is found in the preparation of carbomethoxy-β-hydroxynaphthoyl-β-hydroxynaphthoic acid[2] from β-hydroxynaphthoic acid and the chloride of its carbomethoxy derivative. The coupling is effected by dimethyl aniline in benzene solution.

Finally, as a curiosity, may be mentioned the coupling of carbomethoxyferuloylchloride with *p*-hydroxybenzoic acid by several hours' heating of its solution in acetylene tetrachloride at 110°. The reaction is completed with evolution of hydrochloric acid gas.[3]

The general process, naturally, can also serve for the preparation of mixed forms and it may be mentioned historically that the first coupling of this sort was carried out with *p*-hydroxybenzoic acid, and the chloride of tricarbomethoxygallic acid, whereby the tricarbomethoxygalloyl-*p*-hydroxybenzoic acid resulted.[4]

If the phenolcarbonic acid contains only one hydroxyl group, the course of the reaction is simple. The behavior is naturally more complicated when 2 or 3 hydroxyl groups are present; for not only can isomeric carbomethoxylated didepsides result, but also complicated products, such as derivatives of tri- or tetradepsides. In most investigations which have been carried out in this direction, the product was a mixture whose resolution into its constituents presented difficulty. Only one example was worked out satisfactorily with definite results. This is the coupling of the dicarbomethoxyorsellinic chloride with orsellinic acid,[1] which was necessary for the synthesis of lecanoric acid.

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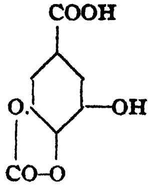
[1] E. Fischer and K. Hoesch, *Ann.*, **391**, 348 (1912).

[2] *Ibid.*, **391**, 355 (1912).

[3] *Ibid.*, **391**, 359 (1912).

[4] *Ber.*, **41**, 2888 (1908).

In other cases, it has been preferable to protect a part of the phenol groups of the phenolcarbonic acids to be coupled, by carbomethoxy groups. As an example, the synthesis of digallic acid serves. Here the chloride of tricarbomethoxygallic acid was coupled, not with free gallic acid, but, with its dicarbomethoxy derivative in alkaline solution,[2] and if, instead of the dicarbomethoxy compound, the carbonylogallic acid[3]



which contained a free hydroxyl in the *m*-position,[4] was used, still better results were obtained.

Another example is the coupling of dicarbomethoxyprotocatechuic acid chloride with monocarbomethoxyprotocatechuic acid in alkaline solution to give diprotocatechuic acid.[5]

According to the former process, in the coupling of a chloride to an *o*-phenol group in alkaline solution, a certain deviation which noticeably decreased the yield was observed, and thus, in many cases, it was impossible to isolate the product. Hence, another modification besides the use of dimethyl aniline was sought.

A satisfactory result was obtained when, instead of the phenolcarbonic acid, the aldehyde was used. The best example of this is furnished by the synthesis of *o*-diorsellinic acid,[6] for which the chloride of dicarbomethoxyorsellinic acid was brought together with *p*-monocarbomethoxyorcyl aldehyde in alkaline solution. The coupled product results in good yield and can be changed easily into tricarbomethoxy-*o*-diorsellinic acid by oxidation with permanganate. I am convinced that equally good results would be obtained with salicylic acid and similar substances.

For the preparation of *o*-didepsides the treatment of *o*-phenolcarbonic acids with phosphorus pentachloride and dimethyl aniline also serves, as is proven by the synthesis of disalicylic acid according to the patent of Böhringer and Son. We have applied the process with success to the monocarbomethoxy derivatives of gentisic acid and β-resorcylic acid, which contain the carbomethoxy group in the *p*-position. In both cases, the coupled product, *i. e.*, the dicarbomethoxy compound of the didepside, could be obtained crystalline.[1]

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[1] E. Fischer and H. O. L. Fischer, *Ber.*, 46, 1138 (1913).

[2] E. Fischer, *Ibid.*, 41, 2890 (1908); E. Fischer and K. Freudenberg, *Ann.*, 384, 242 (1911).

[3] E. Fischer and K. Freudenberg, *Ber.*, 46, 1120 (1913).

[4] *Ibid.*, 46, 1124 (1913).

[5] E. Fischer and K. Freudenberg, *Ann.*, 384, 238 (1911).

[6] E. Fischer and H. O. L. Fischer, *Sitzungsber. d. Berliner Akad.*, 1913, 507.

The carbomethoxy derivatives of the didepsides are as a rule crystalline substances. An exception is the amorphous derivative of digallic acid, which, so far, has resisted all attempts to crystallize it. Also, in other cases (for example with protocatechuic acid), we have given up the isolation of the carbomethoxy derivative, since the didepside itself is more easily purified. The carbomethoxy compounds are true acids and thus decompose alkali bicarbonate and, in general, are easily soluble in dilute potassium bicarbonate solution. This property can be used to advantage as a test of purity and also for separation from other indifferent substances.

The formation of the carbomethoxy didepsides often occurs with nearly theoretical yield. In other cases, this is lowered by side reactions. If the coupling takes place in aqueous alkaline solution, a large part of the chloride can be recovered as the corresponding acid. If the coupling takes place in alkaline acetone solution or in benzene solution with dimethyl aniline, there is obtained a varying quantity of indifferent substances of the nature of acid anhydrides. Their separation is carried out, as above mentioned, by treatment of the crude product with a dilute solution of potassium bicarbonate. Thus it is preferable to dissolve the crude product in a little acetone and then mix with the bicarbonate solution. The carbomethoxydidepside is then later precipitated from the aqueous solution of its potassium salt by mineral acid.

Elimination of the Carbomethoxy Group.

As already mentioned, this can be carried out by cold dilute alkali or by aqueous ammonia. In the first case the alkali carbonate results, in the second, a large part of the carbomethoxy group is split off as urethane.[2] If the depside union is strong enough to resist the action of the alkali for hours then this procedure is best. For this purpose, the carbomethoxy derivative is dissolved in enough *N* alkali to neutralize the carboxy group, and to eliminate the carbomethoxy group a further 2 mols of sodium hydroxide are added. This operation is best carried out at 20° and the reaction is generally ended in $^1/_2$ to $^3/_4$ hour. Only in the preparation of lecanoric acid from its carbomethoxy derivative was the alkali allowed to act for 2 hours, as lecanoric acid itself is very stable towards cold alkali; while with most didepsides, 24 hours' standing with 3 mols excess of *N* sodium hydroxide completely, or largely, splits the compounds into its components.

On account of this sensitiveness towards alkali, aqueous ammonia was used in the majority of cases for splitting the carbomethoxy derivative.

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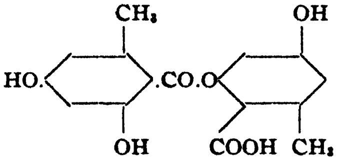
[1] E. Fischer and K. Freudenberg, *Ann.*, 384, 225 (1911)

[2] *Ber.*, 41, 2885 (1908).

Here, also, the action takes place best at 20° and N or $N/2$ solution in large excess was used. Since some of the ammonium salts of the carbomethoxy didepsides are rather insoluble in water, it is preferable, in such cases, to use acetone or pyridine as solvent.

The didepsides so far investigated are crystalline substances, difficultly soluble in cold water, which melt with decomposition, react acid and dissolve in bicarbonate solution. On account of the free hydroxyl group, they give colorations with ferric chloride which are suggestive of those produced by the free phenolcarbonic acids. If, for example, the phenol group is next to a carboxyl then, similarly to salicylic acid, a strong red to blue-violet coloration is observed. This color may not appear, however, if an hydroxyl is next to a depside union, for *p*-diorsellinic acid gives no real purple coloration.



All depsides are split into their components by excess of dilute alkali at room temperature, the reaction velocities differing very greatly.

By diazomethane, the depsides are totally methylated. Esterification of the carboxyl group takes place first and then methylation of the free phenol groups; the hydroxyl next to a carboxyl is attacked most slowly. The resulting, totally methylated, esters are beautifully crystalline substances which melt lower than the depsides and without decomposition. They thus serve very well as a means of characterization and identification of the depsides. As examples, I would cite the products which will be discussed later, namely, the methyl ester of trimethyl-*p*-diorsellinic acid from lecanoric and evernic acids and the pentamethyl-*m*-digallic acid from *m*-digallic acid.[1] If the depsides contain several adjacent phenol groups, as in gallic acid or pyrogallol carbonic acid, they are very sensitive to oxygen in alkaline solution, which deserves attention during their preparation.

The didepsides of gallic, protocatechuic, gentisic and β-resorcylic acids are precipitated by dilute glue solution and give precipitates with quinine acetate or by high dilution. They differ in this respect from the corresponding phenolcarbonic acids and approach the tannins.

Tridepsides.[2]

From monophenol carbonic acids, the theory only admits of the following type of tridepside:

$$HO.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.COOH$$

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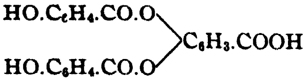
[1] E. Fischer and K. Freudenberg, *Ber.*, **46**, 1127 (1913).

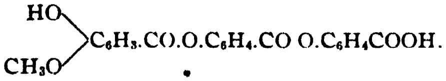
[2] E. Fischer and K. Freudenberg, *Ann.*, **372**, 32 (1910).

If, however, a di- or triphenolcarbonic acid is considered, then the following type is possible:



$$\left.\begin{matrix} HO.C_6H_4.CO.O \\ HO.C_6H_4.CO.O \end{matrix}\right\rangle C_6H_3.COOH$$

Compounds of the second type have not been fully investigated so far. Perhaps to this class belongs a substance which Freudenberg and I[1] obtained as a by-product after saponification subsequent to the action of tricarbomethoxygalloyl chloride on gallic acid in alkaline solution. Our feeling that it is a bisgalloylgallic acid still lacks proof, however, and thus the exact description of our investigation has been delayed. Of the compounds of the first type, two examples are known, the di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid, and the mixed form vanilloyl-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid,



$$\left.\begin{matrix} HO \\ CH_3O \end{matrix}\right\rangle C_6H_3.CO.O.C_6H_4.CO\ O.C_6H_4COOH.$$

The first was obtained by Klepl, along with the didepside, by heating *p*-hydroxybenzoic acid. Freudenberg and I prepared it in beautifully crystalline and apparently pure condition by the new method in the following way:

p-Carboethoxybenzoyl chloride was coupled with *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid in alkaline solution. To split off the carboethoxy group, the product was dissolved in a mixture of acetone and pyridine and ammonia was then added. The tridepside could be obtained in moderately long needles by recrystallization from acetone, while Klepl has described it as a scarcely crystalline powder. In spite of this, we believe that his preparation is identical with our tridepside. The same product could undoubtedly be obtained in a third way, namely by coupling *p*-hydroxybenzoic acid with the chloride of carbomethoxy-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid.

The second mixed tridepside was prepared in an analogous way from carbomethoxyvanilloyl chloride and *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid.

The two tridepsides melt above 200°, are practically insoluble in water and difficultly soluble in most organic solvents. With ferric chloride they give colorations in alcohol solution similar to that of *p*-hydroxybenzoic acid.

Tetradepsides.[2]

Here also two forms are known, the tri-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid,

$$HO.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.COOH,$$

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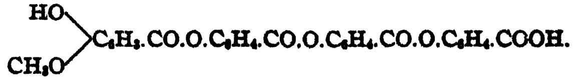
[1] *Ber.*, **45**, 2712 (1912).

[2] E. Fischer and K. Freudenberg, *Ann.*, **372**, 32 (1910).

and vanilloyl-di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid,



$$\left.\begin{matrix}HO\\CH_3O\end{matrix}\right>C_6H_3.CO.O.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.COOH.$$

The first was prepared from carboethoxy-*p*-hydroxybenzoyl-*p*-hydroxybenzoyl chloride and *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid in alkaline solution. For the preparation of the second, carbomethoxyvanilloyl-*p*-hydroxybenzoyl chloride and *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid served.

Here, all operations were rendered difficult by the slight solubility and reactivity of the materials. Both tetradepsides could be obtained crystalline. They are very difficultly soluble in most organic solvents and melt with decomposition.

Under the name of tetra-*p*-oxybenzoide, H. Schiff[1] has described a product that resulted by heating *p*-hydroxybenzoic acid with phosphorus oxychloride, and which has the same composition as the above tetradepside. A repetition of Schiff's experiment has shown that this preparation differs from ours and, thus, we do not believe it can be considered an ordinary polydepside.

Further application of the process to the synthesis of higher depsides has been abandoned on account of the increasing experimental difficulties and because the knowledge of such forms would seem to present no further great interest.

In conclusion I append the following list of depsides prepared by us. The earlier known substances, either artificially prepared or found in nature are designated by an asterisk(*). Those marked by † will be described shortly.

Didepsides.

*Di-*p*-hydroxybenzoic acid (*Ber.*, **42**, 217 (1909)).
Di-*m*-hydroxybenzoic acid†.
*Di-salicylic acid (Salicylo-salicylic acid of Böhringer and Son).
Di-protocatechuic acid (*Ann.*, **384**, 238).
Di-gentisic acid (*Ann.*, **384**, 230).
Di-β-resorcylic acid (*Ann.*, **384**, 233).
p*-Di-orsellinic acid (lecanoric acid) (*Ber.*, **46, 1143 (1913)).
o-Di-orsellinic acid (*Berl., Akad.*, **1913**, 507).
m-Digallic acid (*Ber.*, **46**, 1124 (1913)).
Di-syringic acid†.
Di-*o*-cumaric acid (*Ann.*, **391**, 363).
Di-ferulic acid (*Ann.*, **391**, 362).
Di-β-hydroxy naphthoic acid (*Ann.*, **391**, 356).
p-Hydroxybenzoyl-*m*-hydroxybenzoic acid†.
m-Hydroxybenzoyl-*p*-hydroxybenzoic acid†.
Salicylo-*p*-hydroxybenzoic acid†.
Vanilloyl-*p*-hydroxybenzoic acid (*Ann.*, **372**, 51).

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[1] *Ber.*, **15**, 2588 (1882).

Feruloyl-*p*-hydroxybenzoic acid (*Ann.*, **391**, 360).
α-Hydroxy naphthoyl-*p*-hydroxybenzoic acid (*Ann.*, **391**, 354).
Orsellinoyl-*p*-hydroxybenzoic acid (*Ber.*, **46**, 1141 (1913)).
Protocatechuyl-*p*-hydroxybenzoic acid (*Ber.*, **42**, 1484 (1909)).
Galloyl-*p*-hydroxybenzoic acid (*Ber.*, **41**, 2888 (1908)).
Pyrogallol carboyl-*p*-hydroxybenzoic acid (*Ber.*, **46**, 2396 (1913)).
Syringoyl-*p*-hydroxybenzoic acid†.
p-Hydroxybenzoyl syringic acid†.
Pentamethyl-*m*-digallic acid (*Ber.*, **45**, 2718 (1912)).
Pentamethyl-*p*-digallic acid (*Ber.*, **46**, 1130 (1913)).
Vanilloyl-vanillin (*Ann.*, **372**, 63).

Tridepsides.

*Di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid (*Ann.*, **372**, 38),
Vanilloyl-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid (*Ann.*, **372**, 55).

Tetradepsides.

Tri-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid (*Ann.*, **372**, 43),
Vanilloyl-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid (*Ann.*, **372**, 59).

Lichen Substances.

The only natural sources of the depsides have, until now, been the lichens, those peculiar plant forms, which, according to the discovery of Simon Schwendener, arise through symbiosis of algae and molds. To these singular morphological properties correspond also their peculiar position in chemical respects, and particularly, their content of depsides. Among the latter, the best known is lecanoric acid, which has long been regarded as an ester-like anhydride of orsellinic acid, without anything certain having been found out about the position of the depside group.

Very closely related is evernic acid, which can be regarded, on account of its splitting by bases, as an ester-like anhydride of orsellinic acid and everninic acid. The synthetic investigations which I, in conjunction with my son, Hermann O. L. Fischer,[1] have so far carried out, have been limited to these two acids.

The synthesis of lecanoric acid is carried out in the following manner: After the preparation of the crystalline dicarbomethoxyorsellinoyl chloride had succeeded, this was coupled with orsellinic acid in aqueous alkaline acetone solution at —15° and the resulting dicarbomethoxy compound saponified by a two-hour treatment with excess *N* sodium hydroxide at 20°. Thereby a diorsellinic acid results in good yield and this has proven identical in every respect with a sample of the natural lecanoric acid, which we owe to the kindness of Mr. O. Hesse in Feuerbach.

The final proof of identity rests on a comparison of the change of the natural and the artificial preparations into the methyl ester of trimethyllecanoric acid by diazomethane. This ester possesses a sharp melting point, which was the same for both preparations and also for their mixture.

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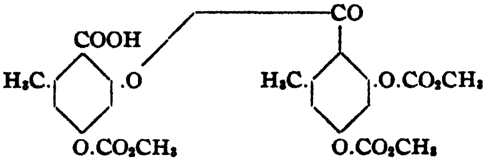
[1] *Ber.*, **46**, 1138 (1913); further, *Sitzungsber. d. Berliner Akademie*, 1913, p. 507.

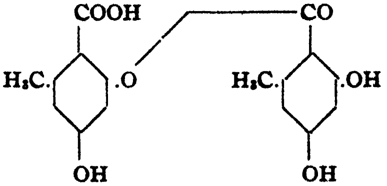
Simultaneously with these investigations, my former co-worker, K. Hoesch[1] has derived orsellinic acid itself from orcyl aldehyde, prepared by the Gattermann synthesis, in which he oxidized the carbomethoxy compound of the latter with permanganate, and then split off the carbomethoxy groups, just as Freudenberg and I[2] recommended for the change from vanillin into vanillic acid.

Besides the synthesis, we could also supply the proof that the depside union was in the *p*-position. This was already probable by the very strong red-violet coloration of the dicarbomethoxylecanoric acid with ferric chloride. Still more conclusive is the preparation of *o*-diorsellinic acid and its difference from lecanoric acid.

For this second synthesis, we first attempted to couple dicarbomethoxyorsellinoyl chloride with the monocarbomethoxyorsellinic acid, which contained the free phenol group in the *o*-position, in alkaline acetone solution. The failure of the experiment caused us to choose the previously mentioned indirect way from monocarbomethoxyorcyl aldehyde. This can be coupled without difficulty in alkaline acetone solution, with dicarbomethoxyorsellinoyl chloride. The tricarbomethoxyorsellinoylorcyl aldehyde resulting, in good yield, can have only the following structure:



By oxidation with permanganate, it is transformed into the tricarbomethoxy *o*-di-orsellinic acid, from which there results, on saponification with dilute ammonia, with very good yield the *o*-di-orsellinic acid.



This differs from lecanoric acid in many properties; in particular by the coloration with ferric chloride, with which it shows in aqueous alcohol solution not the intense purple color but rather a brown-red coloration.

We had hoped that the *o*-di-orsellinic acid would be identical with the gyrophoric acid, which likewise is found in lichens, and which, according to its splitting by alkali, has been held to be isomeric with lecanoric acid. But the comparison of the synthetic preparation with a sample of natural gyrophoric acid, which likewise Mr. O. Hesse most kindly placed at our disposal, has proven their complete dissimilarity, and from this we draw the conclusion that the gyrophoric acid cannot be a didepside of orsellinic acid, but must possess some other constitution. This observation shows how very useful syntheses are in deciding important structural questions in the chapter of the lichen substances.

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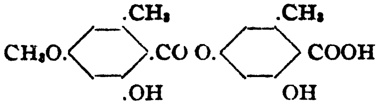
[1] *Ber.*, 46, 886 (1913).

[2] *Ann.*, 372, 68 (1910).

As an other example of this I can cite the structure of evernic acid, which my son and I have cleared up in the following way: The acid, a sample of which we obtained again from Mr. Hesse was, similarly to lecanoric acid, dissolved by an ethereal solution of diazomethane on long standing and shaking and transformed into a beautifully crystalline neutral ester, which we have identified by melting point, mixed melting point, solubility and analysis, with the methyl ester of trimethyllecanoric acid.[1]

Thus evernic acid must be a monomethyllecanoric acid, and since the everninic acid resulting from its hydrolysis is a *p*-methyllecanoric acid,[2] in evernic acid the methyl group must be in the *p*-position to the depside group.

Therefore, this gives, as the only possibility for evernic acid, the following structural formula:



I hope that now the synthesis of evernic acid can also be carried out from everninic acid and orsellinic acid according to the method of synthesis of lecanoric acid.

Tanning Substances.

Under this name are now collected together a large number of plant substances which possess the common property of combining with animal hides. They fall in wholly different groups as soon as one employs a chemical view-point for their classification. Our investigations are limited to the tanning substance of the nutgalls, the so-called tannin, and a few substances belonging to the same type. I can describe them in short as acyl-like compounds of sugar with phenolcarbonic acids.

The history of the tannins, which dates back into the 18th century is so extensive, that I, therefore, must desist from giving it completely here. Thus, I will be content by giving again, with slight amplification what is quoted in the first paper by Freudenberg and myself "On Tannin and the Synthesis of Similar Substances."

Adolf Strecker,[3] on the basis of extended investigations, came to the conclusion that tannin was a compound of glucose and gallic acid, for

[1] The investigation will be published shortly.

[2] E. Fischer and K. Hoesch, *Ann.*, 391, 35 (1912).

[3] *Ann.*, 81, 248 (1852); 90, 328 (1854).

which he derived the formula $C_{27}H_{22}O_{17}$. That would correspond to a combination of 3 mols of gallic acid and one mol of glucose. When he later succeeded,[1] first by silver nitrate or arsenic acid and then also by phosphorus oxychloride,[2] in obtaining a glue-precipitating substance from gallic acid, H. Schiff[2] declared this to be the essential constituent of tannin, gave for it the formula $C_{14}H_{10}O_9$ and named it digallic acid. This formula had been recommended long before by Mulder but was contested by Strecker. The result of Strecker in regard to the formation of glucose from tannin was later substantiated by several investigators; for example Ph. van Tieghem[3] and H. Pottevin,[4] who effected the hydrolysis with the enzyme of *Aspergillus niger*. The results fluctuated noticeably in regard to the quantity of sugar. Further, since, on the other hand, the formation of sugar has been wholly disputed, the view of Schiff has so well maintained itself, that tannin has been represented in the text-books until recently rather generally as digallic acid. In opposition to this, stands its optical activity, which was observed by Ph. van Tieghem, C. Scheibler, Flavitzky and Gunther,[5] and was used by the last as an argument against the formula of Schiff. Experiments are not lacking to remove this theoretical difficulty,[6] but the determination of the molecular weights and the careful observations of P. Walden[7] on the electrical conductivity, the light absorption and the behavior towards arsenic acid, has undoubtedly shown that tannin and Schiff's digallic acid are different. The difference became still greater when I succeeded in obtaining digallic acid in a crystalline condition and establishing its composition with certainty.[8] Meanwhile, M. Nierenstein, from numerous investigations had reached the conclusion that tannin is essentially a mixture of digallic acid and optically active leucotannin. This view cannot stand criticism. It is in opposition to the older observations on molecular weight and acidity of tannin, and our further investigations[9] have not given the

[1] J. Löwe, *J.*, 1867, 446; 1868, 559.

[2] H. Schiff, *Ber.*, 4, 232, 967 (1871); *Ann.*, 170, 43 (1873); *Ber*, 12, 33 (1879); *Chem. Ztg.*, 19, 1680; cf. also the citation on p. 1172; further, the contradictory statements of Freda (*Gazz. chim. ital.*, 8, 9 and 363 (1878) and 9, 327 (1879)) and Biginelli, *Chem. Zentr.*, 1909, II, 1861, 1863; 1910, II, 23; *Gasz chim. ital.*, 39, II (1909); *Rend. Soc. Chim. Ital.*, 11 (1911)

[3] *Annal. d. Sciences naturelles V. Serie Botanique*, 1867, 210.

[4] *Compt. rend.*, 132, 704 (1901).

[5] Cf. historical by E. v. Lippmann, *Ber.*, 42, 4678 (1909).

[6] Cf. Dekker, *Ber.*, 39, 2497 (1906) and Nierenstein, *Ibid.*, 41, 77 (1908); 42, 1122 (1909); 43, 628 (1910).

[7] *Ber.*, 30, 3151 (1897); 31, 3167 (1898). His observations were substantiated and supplemented by Manea (*Diss.*, *Geneva*, 1904).

[8] *Ber.*, 41, 2890 (1908); further, E. Fischer and K. Freudenberg, *Ibid*, 46, 1124 (1913).

[9] E. Fischer, *Ber.*, 41, 2890 (1908); further, E. Fischer and K.F reudenberg, *Ann.*, 384, 225 (1911).

slightest support for the correctness of Nierenstein's conclusions. The same judgment holds for the assertions of R. J. Manning, who claimed to have isolated from tannin a pentaethyl ester of pentagalloyl glucoside, for the preparation described by him is none other than ethyl gallate.[1] In opposition to Nierenstein, K. Feist[2] arrived at the view that tannin was really a compound of glucose and he has expressed the feeling that tannin from Turkish nutgalls is a combination of glucogallic acid with two ester-like bound molecules of gallic acid. As foundation for this view, he used his observation that a crystalline compound of gallic acid and glucose could be isolated from Turkish nutgalls, which he regarded as an α-glucoside of gallic acid or its anhydride.[3]

In the first place, we have accorded to the results of Feist a greater weight,[4] than he really deserves. His complete publication[3] shows that noticeable inconsistencies exist in the analyses, and, above all, shows that the synthetic β-glucoside of gallic acid[5] prepared by H. Strauss and myself differs so greatly from the preparation of Feist that I can no longer regard the latter as a simple glucoside of gallic acid. What Feist in reality had in hand is not yet clear to me.

Of much more importance have proven the statements of Herzig and his students on the origin and splitting of methylotannin and I will later come back to this more fully.

Our first investigation was concerned with the fundamental question whether the glucose found by Strecker and his followers was really a constituent or only a chance impurity of tannin. For this, above all, the purest possible preparation was necessary. Since the earlier known process for the purification of tannin seemed faulty to us, we have worked out a special method. It consists in extracting the aqueous solution of the best technical tannin, saturated with a slight excess of alkali, with ethyl acetate.[6] In the description of the process we were anticipated by Paniker and Stiasny,[7] who discovered it independently. As a particular advantage of the same, we regard the condition that, by it, all real acids or, as we believe, all substances with a free carboxyl are removed. This conclusion is also important for judgment of the structure of tannin, for it appears to me that it contains no free carboxyl and, therefore, cannot be a derivative of a glucosidogallic acid. We have applied the purification process to different kinds of commercial tannin and thereby obtained preparations which we could regard as essentially identical. In addition,

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[1] Cf. H. C. Biddle and W. B. Kelley, THIS JOURNAL, **34**, 918 (1912).

[2] *Ber.*, **45**, 1493 (1912); further, *Chem. Zentr.*, **1908**, II, 1352.

[3] *Arch. Pharm.*, **250**, 668 (1912).

[4] Fischer and Freudenberg, *Ber.*, **45**, 2713 (1912).

[5] Fischer and Strauss, *Ibid.*, **45**, 3773 (1912).

[6] Fischer and Freudenberg, *Ibid.*, **45**, 919 (1912)

[7] *J. Chem. Soc.*, **99**, 1819 (1911).

I will here emphasize the fact that we have used only the tannin thus purified for all the determining experiments and, indeed, a preparation that proved identical with a product prepared from Chinese nutgalls (Zacken-gallen), and for which the specific rotation in 1% aqueous solution was +70° to 75°. That this preparation was entirely homogeneous one cannot state with more certainty, since an essential property of homogeneous bodies, the crystalline habit, has so far not been observed for it. On the other hand, the absence of this property cannot be regarded as a proof for a high degree of impurity, since with such high molecular substances as tannin the crystalline condition is to be regarded as a more than lucky chance.

With the purified preparation we first repeated the investigation of Strecker on the hydrolysis with sulfuric acid; whereby it has become evident that, for the completion of the action with 5% acid, about 70 hours' heating at 100° is necessary, while by use of 11% acid, as Strecker employed 24 hours suffices. We believe that this slow course of the hydrolysis often has hindered the finding of sugar in the control of Strecker's investigation. To this is due the relatively small quantity of sugar noted, which we found as a rule to be between 7 and 8%, while Strecker observed 15 to 22%. That the higher figures of Strecker were due to his different raw material —at that time tannin was prepared preferably from Turkish nutgalls— is highly probable, but can only be decided by new investigations. Besides, we have purified tannin according to other methods, for example through the potassium salt, and on subsequent determination of the sugar reached the same results. Since, finally, control experiments with mixtures of gallic acid and glucose made clear the error of the method employed, there remains no longer any reason to doubt the results of hydrolysis also in the quantitative respect. They led to the conclusion that in the purest tannin investigated by us one mol of glucose is combined with about 10 mols of gallic acid. Naturally the thought occurred to us to isolate intermediate products, in order, from their composition, to secure further data for judging the structure. But these investigations have been completely fruitless, due to the unpleasant properties of these substances which exclude every guarantee of their homogeneity.

Besides gallic acid, no other phenolcarbonic acid has so far been found in tannin, and our own investigations in this respect have given nothing new. The same holds for the hydrolysis with excess alkali, which begins at ordinary temperatures and on exclusion of air yields large quantities of alkali salt of gallic acid in relatively pure condition. Also here it appears to be very difficult to isolate homogeneous intermediate products. Under these conditions, it appeared desirable to proceed in the synthetic way in order to obtain an insight into the structure of the tannins. We have proceeded from the conception that tannin contains no carboxyl and that thus all the gallic acid must be bound as an ester. This condition will be fulfilled if we can regard tannin as an ester-like combination of one mol glucose with five mols digallic acid according to the manner of pentacetyl glucose. Bold as the hypothesis may appear at first glance, it has become the center point of all further investigation and through it has gained in probability. However, we must first choose a more modest goal for the synthesis, the pentagalloyl glucose, as the digallic acid is too difficultly accessible and also because its complicated composition introduces particular difficulty on the experimental side.

Pentagalloyl Glucose.

For the complete acylation of glucose, there have been found until now three methods: (1) Boiling with acid anhydride in presence of sodium acetate or zinc chloride. The best known example is the preparation of pentacetyl glucose, from which results, according to the catalizer used, the α- and β-form. (2) Treatment with acid anhydride in presence of pyridine (Behrend). According to whether one starts with α- or β-glucose, there results the α- or β-form. (3) Treatment with acid chloride in aqueous alkali solution (E. Baumann). The process has only been completely studied for benzoyl chloride, and gives only one pentabenzoyl glucose of m. p. 186–8°. For gallic acid, none of these processes was applicable, and even for the chloride of tricarbomethoxygallic acid the application was excluded in aqueous alkaline solution, because there would inevitably follow the destruction of the carbomethoxy groups. We were thus forced to search for a new process and have found it in the combined action of the chloride with tertiary bases, for which quinoline has proven to serve particularly well. As a solvent we used dry chloroform, the chloride being very easily taken up in this. However, the glucose is especially difficultly soluble in it. But if it was shaken in finely pulverized condition with chloroform, quinoline and a moderate excess of tricarbomethoxygalloyl chloride for 24 hours, complete solution ensued. By precipitation with methyl alcohol, the product of this coupling may be easily isolated. After appropriate purification, there is formed a feathery, colorless, amorphous powder. We have designated it as pentatricarbomethoyxgalloyl glucose. By careful saponification with excess of alkali in aqueous acetone solution at the ordinary temperature, there was obtained from this a tannin which we regarded as pentagalloyl glucose and which now shows surprisingly close similarity to tannin. An essential difference was evident only in optical rotation and the quantity of gallic acid which resulted on hydrolysis with sulfuric acid.

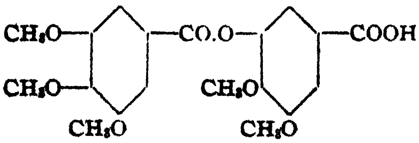
However, I will not be reticent on the difficulty which the establishment of the empirical composition of such amorphous products involves, especially since the percentages for carbon and hydrogen differ only very slightly between pentagalloyl and tetragalloyl glucose. But we have convinced ourselves in simpler cases, for example, in derivatives of benzoic, hydroxybenzoic and salicylic acids, where the analytical differences for penta- and tetraacyl bodies are very much greater, that the process in fact gives the pentaacyl compound, and thus there exists no important ground for assuming that with galloyl bodies the reaction follows another course.

In spite of all this, the homogeneity of pentagalloyl glucose is very doubtful; we hold it rather to be a mixture of two stereoisomers, for the investigation to be cited later, on the benzoylation of glucose in the same way, has shown that different products result, which owe their origin to the α- or β-glucose. Here the pure α- or β-benzoyl glucose can be isolated by crystallization, but the yield and other considerations show that in the crude product there exists a mixture of the two forms. The same could well hold in the case of the galloyl bodies, only here the separation of the pure substances is not possible on account of their amorphous nature.

The pentagalloyl glucose is closely related to tannin in all its properties, so that with its artificial preparation the principal aim of the synthesis seems to be attained. But before one can speak of a complete solution of the tannin question its synthesis also must be realized. How far we have approached to this goal, the investigation on the synthesis of tannin and methylotannin will show.

Methylotannin results, according to the researches of Herzig[1] and his students, from the action of diazomethane on tannin. Since it is wholly indifferent towards alkali, one must assume that it contains neither carboxyl nor free hydroxyl groups. On hydrolysis, it yields according to Herzig, trimethylgallic acid and the unsymmetrical *m,p*-dimethylgallic acid. Combining these observations with the previously advanced conception of the constitution of tannin, the conclusion follows that tannin is essentially an ester-like compound of glucose with five mols *m*-digallic acid, and the corresponding methylotannin the combination of glucose with five mols pentamethyl *m*-digallic acid.

The following investigation on the synthesis of methylotannin rests on these considerations, and demanded large quantities of the hitherto unknown pentamethyl *m*-digallic acid:



This was prepared from trimethylgalloyl chloride and *m,p*-dimethyl ether gallic acid, and for the latter we discovered a new, rather good method of preparation,[1] by coupling in an aqueous alkaline solution.[2] In the same manner the isomeric pentamethyl-*p*-digallic acid[3] resulted from trimethylgalloyl chloride and syringic acid. For differentiating the two isomers, the methyl esters, which have been recently described by Mauthner,[4] serve very well, since they possess sharp melting points.

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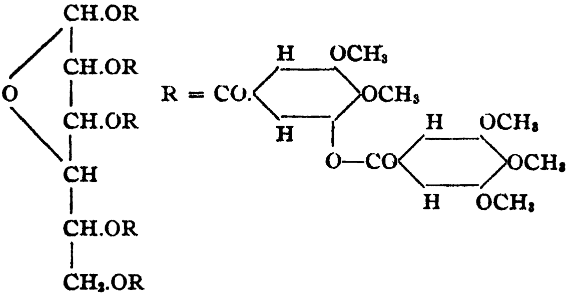
[1] *Ber.*, 38, 989 (1905); *Monatsh*, 30, 543 (1909).

The pentamethyl-*m*-digallic acid yields, further, a beautifully crystalline chloride, and we have coupled this with α- as well as β-glucose, according to the method mentioned before. In both cases products resulted which are to be regarded as penta-acyl derivatives of glucose or, more exactly, as penta-(pentamethyl-*m*-digalloyl)-glucose.



They differ between themselves in optical rotation. Both are dextrorotatory in acetylene tetrachloride and benzene, but the preparation from α-glucose shows a noticeably higher rotation. By repeated resolution the optical rotation changes, and we, therefore of necessity come to the conclusion that both preparations are mixtures, most probably of two stereoisomers, *i. e.*, are derivatives of α- or β-glucose. We have now compared the preparations with a methylotannin, that we prepared from carefully purified tannin from Chinese nutgalls (Zacken-gallen) according to Herzig's directions, and have shown their great similarity, particularly with the preparation from β-glucose, the optical rotation in acetylene tetrachloride is very nearly the same. .

We can scarcely doubt from these observations that the two synthetic penta-(pentamethyl-*m*-digalloyl)-glucoses are very closely related to methylotannin and probably possess the same or very similar structures. But no answer can yet be given as to a final identification; for with these high molecular amorphous bodies the general comparison methods of organic chemistry fail, and we must here, as yet, content ourselves with probabilities. Furthermore, I will not be reticent as to the fact that we have tried also to build up tannin itself artificially from *m*-digallic acid.

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[1] Fischer and Freudenberg, *Ber.*, 45, 2717 (1912).

[2] *Ibid.*, 45, 2718 (1912).

[3] *Ibid.*, 46, 1130 (1913).

[4] *J. prakt. Chem.*, [2] 85, 310 (1912).

To this end, we have first worked out the previously mentioned reliable and satisfactory method for obtaining the acid itself.

We have further proven its structure by complete methylation with diazo methane, *i. e.*, by changing it into the methyl ester of pentamethyl-*m*-digallic acid.[1] We must make here the surprising statement that the first crystallized digallic acid, which according to the synthesis from tricarbomethoxygalloyl chloride and 3,5-dicarbomethoxygallic acid appeared to be the *p*-compound,[2] has not this structure, but probably consists chiefly of *m*-digallic acid.[3] For, complete methylation yields every time the methyl ester of pentamethyl-*m*-digallic acid, m. p. 128°. The results show again how important complete methylation is for comparison of complicated depsides.

We have tried, further, to change *m*-digallic acid into its pentacarbomethoxy compound. The reaction appeared to succeed with chlorocarbonic methyl ester and dimethyl aniline, and later the acid was isolated from the crude product by careful treatment with alkali bicarbonate But now the difficulties began. We have in no way succeeded in obtaining the carbomethoxy compound crystalline, and the chloride derived from it also remained amorphous. Therefore, the finally attempted coupling with sugar was so unsuccessful that we cannot speak of any exact results. The synthesis of tannin in the meaning intended by us, which I hoped to be able to announce to you today, is thus as yet an unsolved problem.

Also the question of structure is not thoroughly answered. One can only say that our hypothesis is as yet the best expression for the observations. But it must not be forgotten that the results of elementary analysis, or of hydrolysis, give no certain differentiation between a compound of glucose with 9, 10 or 11 mols gallic acid, respectively.

To this is also added the uncertainty whether tannin, after the best purification, is homogeneous. It could just as well be a mixture of very similar substances, for example a penta-(digalloyl)-glucose with a tetra-(digalloyl)-glucose or tri-(digalloyl)-di-(galloyl)-glucose, etc.

Further, it is possible, if not also probable, that the tanning substance contains in place of glucose one of its polysaccharides.

Finally I must, in order to obviate misunderstanding, again emphasize the fact, that our observations have been limited to the tannin from Chinese nutgalls (Zacken gallen), which today seems to be the chief constituent of commercial tannin. It is thus not excluded that other relationships of sugar and gallic acid will be encountered, with tannins of other origin, for example, that from Turkish nutgalls.

In fact, according to the latest experiments of Dr. Freudenberg, a tannin from the so-called Aleppo-gallen (Merck), purified by the above process, shows noticeable differences. It is slightly levorotatory in aqueous solution and gave, on hydrolysis, more than 10% glucose.

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[1] E. Fischer and K. Freudenberg, *Ber.*, 46, 1127 (1913).

[2] *Ibid.*, 41, 2890 (1908); *Ann.*, 384, 225 (1911).

[3] *Ber.*, 46, 1118 (1913).

But all these questions are of inferior signification, in comparison with the proof that the synthetic pentagalloyl glucose is a tanning substance of the tannin class.

Other Natural Tanning Substances of the Tannin Class.

There are numerous examples of sugar-containing tanning substances. But in the majority of cases treated, they are amorphous, slightly investigated products; many of them appear to be true glucosides,[1] particularly those which yield on hydrolysis aromatic phenol ketones. On the other hand, those which contain phenolcarbonic acids as constituents, appear not to be glucosides but, like tannin, to be ester-like derivatives of sugar. To this class belong, first of all, two crystalline tanning substances, the chebulinic acid of myrabolans and the Hamamelis-tannin crystallized by Gruttner in Böhm's laboratory, with which we have carried out some experiments. The first, which according to H. Thoms is identical with the "eutannin" recently introduced in the trade, yields, under exactly the same conditions as tannin, by hydrolysis with sulfuric acid, glucose which we have proven with all certainty.[2] However, the quantity of gallic acid is noticeably small. Apparently the tanning material is an incompletely acylated compound of glucose, or one of its polysaccharides, and gallic acid. Recently, the investigations of H. Thoms and his student, W. Richter, on eutannin,[3] have appeared, and contain many valuable observations, but leave the sugar content of the tanning substance doubtful. On the other hand, I must say that I cannot assent to the speculations thus founded. The chebulinic acid demands a new, complete, investigation before one can pronounce a final judgment on its structure.

The Hamamelis-tannin also gives, on hydrolysis with sulfuric acid, a sugar which is entirely different from glucose, and appears to be a hitherto unknown body.[4]

These observations show that the tanning substances can also be a source for new members of the sugar series. Dr. Freudenberg will exhaustively investigate the sugar of Hamamelis-tannin.

Whether the crystalline tanning substance of tea described by A. W. Naninga[5] also belongs here, is still to be proven.

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[1] The earlier custom of calling all natural derivatives of glucose, which are not simple carbohydrates, glucosides, cannot be retained. I regard as glucosides only those substances which are similarly constituted to the methyl or phenyl glucosides.

[2] E. Fischer and K. Freudenberg, *Ber.*, 45, 918 (1912)

[3] Work of the *Pharmazeut. Institut d. Univ. Berlin*, 9, 78, 85 (1912).

[4] E. Fischer and K. Freudenberg, *Ber.*, 45, 2712 (1912).

[5] *Mededeelingen uit's Lands Plantentuin Nr*, 46; *Onderzoekingen betreffende de Bestanddeelen van het Theeblad.*

Generalization of the Tanning Material Synthesis.

The process which served for the building up of pentagalloyl glucose is easily applicable to other phenolcarbonic acids. As has been mentioned before, the penta-*p*-hydroxybenzoyl-glucose[1] was so obtained. It is very difficultly soluble in water and its elementary analysis undoubtedly shows it to be a penta-acyl compound. The pentasalicyloglucose which will be fully described in a later publication, possesses entirely similar properties. Just as difficultly soluble in water is the corresponding derivative of caffeic acid, which I had Mr. R. Oetker[2] prepare. The compound of pyrogallolcarbonic acid, which we have designated as pentapyrogallol carboylglucose,[3] has proven particularly interesting. It is isomeric with pentagalloyl glucose and shows in general the same behavior, although it shows a noticeable difference in its solubility in water. While the galloyl compound is easily taken up in cold water, the isomeric substance is very difficultly soluble in hot water and is practically insoluble in cold water. The same also holds for its dark colored iron compound.

On first glance, this difference in substances of so similar a structure as the two tanning materials, appears very surprising. But it loses in significance when one remembers that tannin and also the similar pentagalloyl glucose are inclined to form colloidal aqueous solutions. This property is present only to a slight degree or not at all in the isomeric compound. Such observations merit attention for the study of colloidal solutions, for they show how dependent their formation is on small differences in the structure of the materials. On the other hand, the formation of hydrosols is of highest importance for the role which such substances play in the living world, and this applies also to their chemical characteristics, as proven by the case of the pentagalloyl glucose; for here it was not easy, on account of the difficulty in preparing aqueous solutions, to verify the astringent taste and the precipitation by glue solution.

For all the above-mentioned glucose derivatives, the same thing holds, as I have before drawn attention to in connection with the homogeneity of pentagalloyl glucose, *i. e.*, they are probably mixtures of the two stereoisomeric derivatives of α- and β-glucose.

Like the sugars, the phenolcarbonic acids can be coupled with the true glucosides, as the preparation of the tetragalloyl α-methylglucoside has proved.[4] That this also shows the characteristic properties, for example, the taste and the precipitation phenomena of tanning substances, is not surprising, since it is well known that ethyl gallate shows noticeable precipitability by glue solution. With the methyl glucoside derivatives there is obviously missing the complication which arises, as in the glucose derivatives, from the simultaneous formation of α- and β-forms.

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[1] E. Fischer and K. Freudenberg, *Ber.*, 45, 933 (1912).

[2] Will be published shortly.

[3] E. Fischer and M. Rapaport, *Ber.*, 46, 2397 (1913).

[4] Fischer and Freudenberg, *Ibid.*, 45, 934 (1912).

According to the behavior of methylglucoside, it cannot be doubted that the simple polyhydric alcohols will serve for the same synthesis. We have so far combined only glycerol[1] with gallic acid, submitting the product merely to a hasty investigation, since such bodies exhibit no particular interest.

Benzoylation and Cinnamoylation of Sugars and Polyhydroxylated Alcohols.

By the application of the new acylation method to the simple aromatic chlorides, some new and noteworthy results were obtained. The benzoylation of glucose has been carried out formerly only in aqueous alkaline solution, giving as a final product a pentabenzoyl glucose which melted at 186–8°, and for which I, in conjunction with B. Helferich, found in chloroform solution $[\alpha]_D^{20} = 25.4°$.[2] But the yield of this high melting preparation was very unsatisfactory (about 15% of the theory). A preparation of about the same rotation and similar melting point can be obtained with a much better yield, according to the new process, by shaking β-glucose with a mixture of benzoyl chloride, quinoline and chloroform. On the other hand, α-glucose gave, under the same conditions, an isomeric pentabenzoate with a much higher rotation, $[\alpha]_D^{20} = 107.6°$, whose melting point, however, was rather inconstant.[3]

That steric rearrangement takes place from the α- to the β-form or conversely, was quite probable according to the resulting yield, and was proven by the following experiment: A mixture of α-glucose, benzoyl chloride, quinoline and chloroform, in the proportions used earlier, remained standing 20 days after complete solution had taken place. There had then separated a rather large quantity of crystalline β-pentabenzoyl glucose.

Still easier than the benzoylation, is the cinnamoylation of sugar with cinnamic acid chloride and quinoline. I have prepared with Mr. R. Oetker, in this way, the pentacinnamoyl derivatives of α- and β-glucose, galactose, mannose, and the hexacinnamoyl mannite. They are all beautifully crystalline substances. By this process, the pentabenzoyl and pentacetyl mannose (m. p. 114–6°; $[\alpha]_D^{20} = -24.8°$) were obtained crystalline. The detailed description of this investigation will soon follow.

Experiments on the Partial Acylation of Sugar and Polyhydroxylated Alcohols.

All the previously mentioned acylation experiments were directed towards the preparation of the end product and thus were carried out with an excess of acid chloride. To conduct the reaction only to an intermediate stage, the experimental conditions are also unfavorable; for the sugar on shaking goes gradually into solution in the acylating liquid and is thus at the beginning in contact with an excess of the chloride.

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[1] Fischer and Freudenberg, *Ber.*, **45**, 935 (1912)

[2] *Ann.*, **383**, 88 (1911).

[3] *Ber.*, **45**, 2725 (1912).

In other methods of acylation, for example, by acetylation with acetic anhydride or benzoylation according to Baumann, it is just as difficult to isolate partially acylated sugars in pure condition. One must, therefore, seek for a new method for the preparation of such products, and here reflection suggests the partial protection of the hydroxyls of the sugar by other groups which afterwards can be easily split off again. The acetone derivatives of the sugars and polyhydric alcohols, which were discovered by me, appear to be particularly useful for this purpose. Some years ago, I carried out such experiments with acetone-glycerol,[1] in order to prepare a monobenzoyl derivative with benzoyl chloride in alkaline solution. Unfortunately, the results were negative; for, under the conditions chosen, the acetone residue was split off and tribenzoyl glycerol formed. Perhaps this splitting can be avoided by excluding water according to the new acylation method, and I am already occupied in this direction. If, in such a way, the partial coupling of sugars with phenolcarbonic acids can be realized, just as Irwin has recently succeeded in the partial methylation of glucose, it will mark an important advance in the synthesis of tanning substances. For, as I have mentioned before, chebulinic acid probably belongs in this class of partially acylated sugars, and it is to be hoped that the same is the case with many other natural products which are easily soluble in water, and thus differ from the completely acylated glucose derivatives, which are as a rule difficultly soluble.

Physiological and Practical Significance of the Synthesis of Tannins.

The knowledge that ester-like compounds of sugar and phenolcarbonic acids form a great class of tannin-like tanning substances, is doubtless of importance to the plant physiologists. Especially interesting appears to me the fact that the sugar of plants can be used for esterification just as well as glycerol or the monohydric alcohols. The organism tolerates free acid, in general, only at definite places, as in the maw of animals or in unripe fruits, or in bark and shells, where they probably act as defensive agents. Generally it endeavors to neutralize the acid group. This happens often by salt formation, but much oftener by amide formation, as in the proteins, or by ester formation, as in the fats. Under this now comes the esterification of sugars. Since sugars are much more widely distributed than glycerol, I do not doubt that such ester derivatives will be met still oftener in the plant kingdom and perhaps in the animal kingdom also.

I have in mind not alone the phenolcarbonic acids, but more especially the numerous hydroxy acids of plants. That one has so far overlooked their sugar derivatives, does not surprise me, since they are probably easily soluble and easily saponified bodies. It has long been my wish to prepare such combinations synthetically, but the method for this must first be found. Probably the carbomethoxy derivatives recently discovered by me and my son will play a part in it.[1] Previously I had to be contented with directing the interest of plant physiologists to these things. Perhaps we will find such esters in sweet fruits, which, in the unripe condition, contain noticeable quantities of glycollic acid and its homologs. I have myself carried out some experiments on this point, but so far without decisive results. I hope, later, to be able to communicate more definitely on this as well as on the unequal distribution of acids in the shell and meat of certain fruits, for example, the early plums.

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[1] *Ber.*, 28, 1170 (1895).

Both the naturalist and the synthetic chemist are often confronted by the question as what practical purpose the results of his work can serve, and to myself in a circle of scholars, as I exhibited the artificial tannin and an ink prepared from it, which aside from the water was entirely synthetically derived, the question was put: Is it cheaper than the ordinary ink? The answer was naturally negative, and so it must be also for the synthetic tanning substance, so far as concerns its use in the tannery; for here only very cheap substitutes, such as the recently introduced neradol of Stiasny, come into consideration.

But the matter appears otherwise when we consider that tannins in small quantities are constituents of important comestibles, such as wine, tea, coffee and numerous sweet fruits, on whose taste it has an influence not to be underestimated. If once synthetic chemistry breaks into this important field, of which I have no doubt, then, probably the synthesis of tanning substances will be honored also in its technical applications.

High Molecular Substances.[2]

Among the before-mentioned products of the tannin synthesis many substances of rather high molecular weight are found; for with the penta-(tricarbomethoxy galloyl) glucose this total amounts to 1810, and for the penta-(pentamethyl-*m*-digalloyl) glucose it rises to 2051; which has given the inducement to apply this smoothly running ester formation with the members of the sugar group to still more complicated acids. For this purpose the higher fatty acids at first appear particularly useful, such as, stearic, behenic and melissic, but finally we have found, in the derivatives of gallic acid, especially its tribenzoyl compound, a still better material; it yields a beautifully crystalline chloride, which can be completely purified and can be prepared comparatively easily in large quantity. By combination with mannite a neutral ester was prepared which has a molecular weight of 2967. The verification of the composition of such substances is rendered very difficult by the condition that the analytical differences for carbon and hydrogen are not sufficiently great to determine the number of acyl groups with certainty. On this account we have incorporated in the molecule halogenated groups, in order to have the percentage of halogen as a measure for the molecular weight of the final product. For this purpose, we have used the *p*-iodophenyl maltosazone, which on the one hand is distinguished by its fine crystalline state, and on the other hand by a high content of halogen (33%). Its coupling with tribenzoylgalloyl chloride yielded hepta-(tribenzoylgalloyl)-*p*-iodophenyl maltosazone, which, though amorphous, still possesses very fine properties, and on analysis gave such sharp figures that we have no hesitation in proclaiming it as a chemical individual. Its structure follows from the snythesis and corresponds to the following formula, in which R denotes the tribenzoyl gallic acid:

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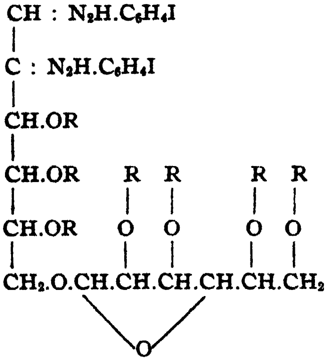
[1] *Ber.*, 46, 2659 (1913).

[2] E. Fischer and K. Freudenberg, *Ber.*, 46, 1116 (1913).



$$\begin{array}{l} CH : N_2H.C_6H_4I \\ | \\ C : N_2H.C_6H_4I \\ | \\ CH.OR \\ | \\ CH.OR \quad\ \ R \quad R \qquad R \quad R \\ | \qquad\qquad\ \ | \quad\ | \qquad\ | \quad\ | \\ CH.OR \quad\ \ O \quad O \qquad O \quad O \\ | \qquad\qquad\ \ | \quad\ | \qquad\ | \quad\ | \\ CH_2.O.CH.CH.CH.CH.CH.CH_2 \\ \qquad\quad \diagdown \qquad\quad \diagup \\ \qquad\qquad\quad O \end{array}$$

$R = CO.C_6H_2(O.CO.C_6H_5)_3$

Hepta-(tribenzoyl galloyl)-*p*-iodophenyl-maltosazone, $C_{220}H_{142}O_{58}N_4I_2$. (Molecular weight 4021.)

The only uncertainty in the formula is the structure of the maltose residue, *i. e.*, the coupling of the two glucose residues, a question, which in the foregoing case has no significance. The molecular weight amounts to 4021. The substance with this molecular weight stands at the head of all organic substances of known structure derived wholly by synthesis.

We have finally proven, by freezing point determination in bromoform solution, that it, as well as a moderately closely related substance, for example, hexa-(tribenzoyl galloyl)-mannite, still satisfactorily obeys Raoult's law. The hepta-(tribenzoyl galloyl)-*p*-iodophenyl-maltosazone exceeds in molecular weight the highest product of the polypeptide synthesis, the *l*-leucyl-triglycyl-*l*-leucyl-triglycyl-*l*-leucyl-octaglycyl-glycine, by more than three times, and I believe, that it is also superior to the majority of natural proteins. However, for the beautifully crystalline oxyhemoglobin, as is well known, a molecular weight of 16,000, has been derived from its iron content, but against such calculations the objection can always be made, that the existence of crystals in no way guarantees chemical individuality, particularly since it can be regarded as an isomorphous mixture, such as the mineral kingdom so often presents to us in the silicates. Such objections vanish with synthetic products, whose formation can be controlled by analogous reactions.

The molecular physicists would do well in the study of high molecular substances to confine themselves to the synthetic products of known structure. I will continue the experiments on the building up of giant molecules with the aid of the processes described.

Certainly it offers in other respects a great incentive to test the productiveness of our methods. As is well known, the modern physicist is endeavoring to split up matter into smaller and smaller pieces. One is long since past the atom, and how long the electrons will be for us the smallest particles of matter, cannot be predicted. It seems to me that organic synthesis is called upon to accomplish the converse, *i. e.*, to accumulate larger and larger masses in the molecule, in order to see how far the compression of matter can go, in the meaning of our present conceptions.[1]

I hope that the results to date will give an effective stimulus in this direction.

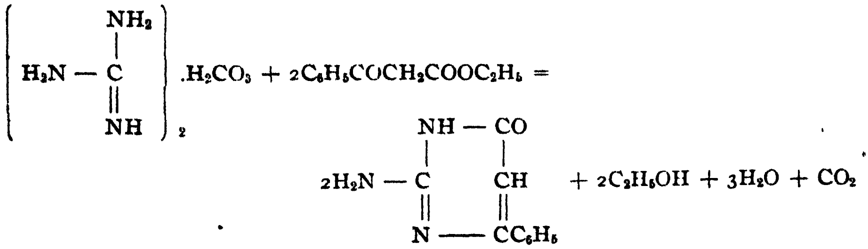
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON PYRIMIDINES. LXX. THE ISOMERISM OF 4-PHENYLISOCYTOSINE.

BY TREAT B. JOHNSON AND ARTHUR J HILL.

Received March 23, 1914.

Jaeger[2] observed, in 1891, that guanidine carbonate and ethyl benzoylacetate interact smoothly, when heated in alcoholic solution, with formation of 2-amino-4-phenyl-6-oxypyrimidine (4-phenylisocytosine, (I) melting at 294°. The reaction may be expressed as follows:



$$\left(\begin{array}{c} NH_2 \\ | \\ H_2N - C \\ \| \\ NH \end{array}\right)_2 .H_2CO_3 + 2C_6H_5COCH_2COOC_2H_5 =$$

$$\begin{array}{rcl} & NH - CO & \\ & |\qquad | & \\ 2H_2N - & C \qquad CH & + 2C_2H_5OH + 3H_2O + CO_2 \\ & \|\qquad \| & \\ & N - CC_6H_5 & \end{array}$$

(I)

Warmington[3] later reinvestigated this reaction and made the interesting observation that this pyrimidine, melting at 294°, is not the only product formed, and succeeded in isolating a second isomeric modification of the pyrimidine (I), which melted at 272–274°. The conditions under which this interesting substance was obtained are discussed in the experimental part of this paper. He also prepared the pyrimidine melting at 294° by heating 2-thio-4-phenyl-6-oxypyrimidine (II) with ammonia.

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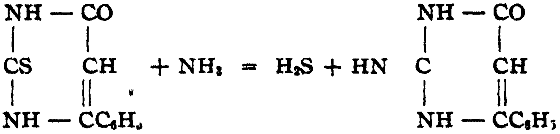
[1] Cf. H. Crompton, *Proc. Chem. Soc.*, 28, 193 (1912).

[2] *Ann.*, 262, 372.

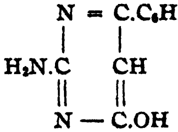
[3] *J. prakt. Chem.*, [2] 47, 214 (1893).



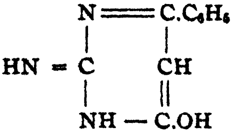
(II) (I)

Warmington showed that the two bases differed decidedly in their solubility and crystalline habit, and concluded that they combined with hydrochloric acid, giving different salts, which he represented by the formulas $(C_{10}H_9ON_3)_2.HCl$ and $(C_{10}H_9ON_3)_2.HCl.H_2O$, melting at 269° and 276–277°, respectively. The two bases were recovered unaltered by decomposing their respective hydrochlorides with alkali. Both pyrimidines gave the same picrate melting at 241°, and also the same acetyl derivative melting at 248°. While the picrate underwent decomposition with alkali, with regeneration of the two isomeric pyrimidines, on the other hand, the acetyl derivative underwent hydrolysis, giving that modification which melts at 294°.

Warmington found that both bases were converted smoothly into 4-phenyluracil by hydrolysis with hydrochlorc acid or by interaction with nitrous acid, and also made the remarkable observation that the modification melting at 294° can be transformed into the base melting at 272° by heating with alcohol or alcoholic ammonia at 180°. In summarizing his observations he wrote as follows: "Auf Grund dieser Versuche konnte wohl kein Zweifel bestehen, dass die eben besprochenen Verbindungen tautomerer Art sind. Ihren Eigenschaften werden, wie schon erwähnt, vielliecht folgende Formeln am besten entsprechen: Da



(III)



(IV)

dieselben jedoch unter dem Einfluss der Reagentien mit der grössten Leichtigkeit in einander übergehen, so ist es vorläufig unmöglich, die eine oder die andere Base mit der ihr zukommenden Formel bestimmt zu belegen."

In all our previous work on guanidine-pyrimidine condensations, we have never encountered any cases of isomerism like this described by

Warmington. It has been our experience that two such formulas as represented by (III) and (IV) represent a single, chemical individual, and consequently it was of especial interest to us to determine whether Warmington had correctly interpreted his experimental results. So far as the writer is aware, no one has hitherto attempted to confirm his work. We have now repeated that part of Warmington's investigation, which deals with the chemistry of 4-phenylisocytosine, and have obtained some very surprising and unexpected results. Not only have we found that some of Warmington's conclusions were incorrect, but we have also obtained new data, which have revealed the most remarkable case of isomerism so far recorded in the pyrimidine literature. A preliminary report of this investigation is now recorded in this paper.

We have applied Warmington's reaction according to his own directions, and have confirmed his observations by isolating his two isomeric modifications of 4-phenylisocytosine. We found, however, that they melt somewhat higher than the temperatures recorded by him. The pyrimidine, which he found to melt at 294°, melts at 303° and the isomeric modification melts at 279–280°, instead of 272°. The product melting at 303° we have designated as the γ-modification, and that form which melts at 279° as the δ-modification of 4-phenylisocytosine. Our reasons for adopting this method of distinguishing between these two isomeric bases will be disclosed below. Both pyrimidines dissolve in cold sodium hydroxide solution and are reprecipitated unaltered by addition of an amount of hydrochloric acid sufficient to neutralize the alkali. If an excess of acid is added, the bases combine immediately, giving their corresponding hydrochlorides.

Warmington concluded that the hydrochlorides of these two bases are different substances. We find that his interpretation of their constitution was incorrect and that the two isomers combine with hydrochloric acid, giving the same salt. It is a monohydrochloride, containing one molecule of water of crystallization, $C_{10}H_{10}ON_3Cl.H_2O$, and melts at 266° with decomposition. Warmington also observed that the two bases were recovered unaltered by decomposing their hydrochlorides with alkali. We now find that the γ-modification, melting at 303°, is the stable form of the pyrimidine and is obtained by decomposing our hydrochloride with alkali. In other words, the δ-form of the pyrimidine undergoes transmutation into the γ-modification when treated with hydrochloric acid. A mixture of the two modifications melted at the same temperature as the stable γ-modification, namely, 303°. Microphotographs of these two modifications of 4-phenylisocytosine are represented in Figs. 3 and 4.

Warmington and Jaeger[1] condensed guanidine with ethyl benzoylacetate under one condition only, namely, by digesting the carbonate of the base with the β-ketone ester in alcoholic solution. It was, therefore, of especial interest to us to examine the behavior of the ketone ester towards guanidine, when digested in alcoholic solution in the presence of sodium ethylate. We have now effected the condensation under such conditions and have made the unexpected and most remarkable observation that an entirely different modification of 4-phenylisocytosine is a product of the reaction. We have designated this as the α-modification of 4-phenylisocytosine whose microphotograph is represented in Fig. 1. It melts at exactly the same temperature (279–280°) as the δ-modification of 4-phenylisocytosine described above, but the experimental evidence indicates that they are not identical substances. The δ-modification can be repeatedly recrystallized from alcohol without any apparent change. On the other hand, the α-modification undergoes a remarkable transformation, when subjected to the same treatment, and is converted into a fourth modification of 4-phenylisocytosine, which melts at 303°. The microphotograph of this new β-modification of the pyrimidine is represented in Fig. 2. The striking difference in the crystalline habit of the two modifications (β- and γ-) is apparent by comparison of their respective microphotographs. They also differ in their solubility in alcohol. Mixtures of the two modifications melt at 303°.

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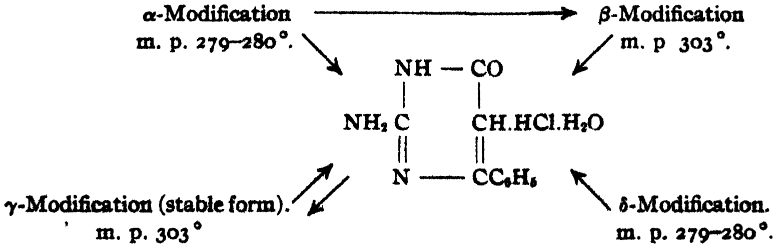
[1] *Loc. cit.*

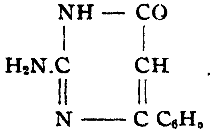
The α- and β-modifications of 4-phenylisocytosine are stable in the presence of alkali and are reprecipitated unaltered from alkaline solutions by the addition of hydrochloric acid. Both pyrimidines are converted into the same hydrochloric acid salt as is formed by dissolving the γ- and δ-modifications of 4-phenylisocytosine in this acid. In other words, they are both transformed by the action of the acid into the hydrochloride of the γ-modification. By treatment of the hydrochloride from either the α- or β-modifications with ammonia the difficultly soluble γ-modification, melting at 303°, deposited immediately. Therefore the α-, β- and δ-modifications of 4-phenylisocytosine can all be transformed into the γ-modification by conversion into their hydrochlorides and then decomposing this common salt with alkali (ammonia). These unique and interesting relationships are represented below. The melting points of the possible mixtures of the four different modifications are recorded in the experimental part of this paper.



$$\begin{array}{ccc} & \mathrm{NH} - & \mathrm{CO} \\ & | & | \\ \mathrm{NH_2} & \mathrm{C} & \mathrm{CH.HCl.H_2O} \\ & \| & \| \\ & \mathrm{N} - & \mathrm{CC_6H_5} \end{array}$$

Regarding the constitution of these four isomers, practically nothing definite can be concluded from the available data. Two general and characteristic properties, however, are very suggestive; namely, that all four modifications are stable in alkaline solutions, and that all four forms combine with hydrochloric acid to give the same salt. It is not improbable that we are dealing simply with an unique case of physical isomerism. To express the chemical differences of the four modifications by correct stereochemical formulae is indeed a difficult matter, when one takes into consideration the great number of possible tautomeric formulae, which can be assigned to 4-phenylisocytosine. It is possible that unknown chemical differences may be revealed by the application of physico-chemical methods of research which will suggest structural differences, but it is true, that our present knowledge does not justify the adoption of definite structural formulas for the four compounds. The study of these isomers and of other closely related pyrimidines will be continued.

Experimental.



The α- and β-Modifications of 2-Amino-4-phenyl-6-oxypyrimidine (4-Phenylisocytosine), .—The α-modification of this pyrimidine is obtained by condensation of guanidine with ethyl benzoylacetate, in the presence of sodium ethylate. The following description of an experiment comprises the necessary information for preparing the base: Eight and nine-tenths grams of sodium were dissolved in 120 cc. of absolute alcohol, and 27 g. of guanidine thiocyanate (3 molecular proportions) and 15 g. of ethyl benzoylacetate added to the cold solution. The mixture was then digested on the steam bath for 10 hours. At the end of this time a thick magma of the sodium salt of the pyrimidine was obtained. The alcohol was then evaporated in an open dish and the residue finally dissolved in the least possible volume of cold water. This solution was then carefully acidified with cold dilute hydrochloric acid in order to precipitate the pyrimidine. Care must be taken here to avoid adding any excess of the acid, in order to prevent the formation of the hydrochloric acid salt. The pyrimidine sometimes separated as an oil, which finally solidified on cooling. At other times it separated at once in a granular condition. The yield of the base is not good, seldom exceeding 3 g. from 15 g. of the β-ketone ester. This product was purified by crystallization from absolute alcohol and deposited in tabular crystals which melted at 279–280° with effervescence (Fig. 1). The pyrimidine is soluble in hot water and sodium hydroxide solution, and is precipitated unchanged from its alkaline solutions by addition of acids.

Calc. for $C_{10}H_9ON_3$: N, 22.46; found (Kjeldahl): N, 22.34, 22.31.

The β-Modification.—Especially characteristic was the behavior of the above α-modification when heated in alcoholic solution. After long boiling and subsequent cooling of the solution, it was observed that the α-form underwent a quantitative transmutation into a modification melting sharply at 303° with effervescence. This is designated as the β-modifications of the pyrimidine and its crystalline habit is represented in Fig. 2. That this raise of the melting point, by this treatment, is not to be explained by removal of impurities, is established by the facts that the 279–280° and 303° products contain absolutely the same amount of nitrogen. A mixture of the two modifications melts sharply at 303°. The lower melting α-modification therefore apparently undergoes a rearrangement when heated with the β-modification. It was also observed that the α-modification slowly undergoes transformation into the higher melting form on long standing at ordinary temperature. The β-form possesses properties much in common with those of the α-modification. A microphotograph of the β-modification is shown in Fig. 2:

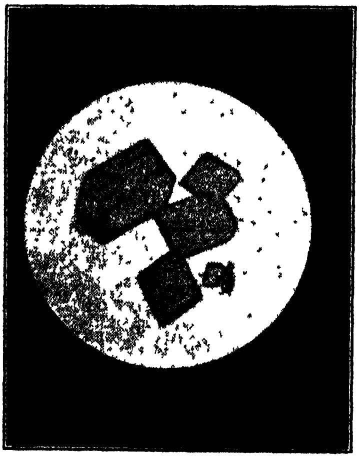


Fig. 1.—α-Modification of 4-phenylisocytosine crystallized, from alcohol. Magnified.

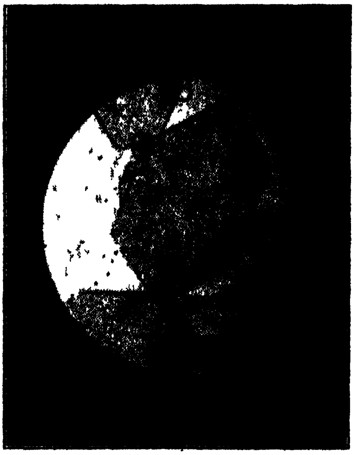


Fig. 2.—β-Modification of 4-phenylisocytosine, crystallized from alcohol. Magnified.

Calc. for $C_{10}H_9ON_3$: N, 22.46; found (Kjeldahl): N, 22.34, 22.39.

The Hydrochlorides of the α- and β-Modifications of 2-Amino-4-phenyl-6-oxypyrimidine.—Both of these modifications dissolved in warm hydrochloric acid and were converted into the same hydrochloride. This crystallized from hydrochloric acid in hair-like crystals which melted at 266° with effervescence. A mixture of the two salts melted at the same temperature. This salt contained one molecule of water of crystallization. Attempts, however, to correctly determine the water by heating at 100°

were unsuccessful. The salt underwent partial dissociation at this temperature with loss of hydrochloric acid and consequently the analytical results were always too high. Analyses of the dehydrated salts showed that the nitrogen content varied between that of the free base and its anhydrous hydrochloride, as would be expected.

ANALYSES.

	N.		H_2O (at 104°).		Cl.	
	Calc.	Found.	Calc.	Found.	Calc.	Found.
Hydrous α-hyd. chl	17.39	17.27	7.45	7.72	...	...
$C_{10}H_{10}ON_3Cl.H_2O$		17.56	..	10.42	...	...
After heating to 104°	18.79	19.73	..	...	...	...
$C_{10}H_{10}ON_3Cl$						
Hydrous β-hyd. chl	17.39	17.34[1]				
$C_{10}H_{10}ON_3Cl.H_2O$		17.47[1]	..	...	14.70	14.89

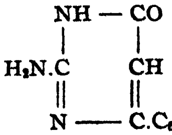
The β-modification showed the same behavior on heating at 100° as that observed in the case of the α-modification.

The Action of Alkali on the Hydrochlorides of the α- and β-Modifications.—When the hydrochloride, which is formed from either of these two bases, is treated with the required amount of alkali (NH_4OH) to neutralize the hydrochloric acid, neither the α- nor the β-modification is precipitated. A third modification of the aminopyrimidine is obtained, which melts at 303° with effervescence. This base is far less soluble in alcohol than either the α- or β-modification, and crystallizes in characteristic, slender prisms. We have designated this as the γ-modification of 2-amino-4-phenyl-6-oxypyrimidine and its crystalline habit is shown in the microphotograph represented by Fig. 3.

Calc. for $C_{10}H_9ON_3$: N, 22.46; found (Kjeldahl): N, 22.50, 32.21.

Behavior of the α- and β-Modifications of the Pyrimidine towards Alkali.—While these two modifications are transformed into the hydrochloride of the γ-modification by solution in hydrochloric acid, they are absolutely stable in alkaline solution. Both forms dissolve in cold, dilute sodium hydroxide solution. On acidifying these solutions with hydrochloric acid the α- and β-forms are regenerated unaltered and melt at 279–280° and 303°, respectively. This stability in alkaline solutions is very remarkable.

The γ- and δ-Modifications of 2-Amino-4-phenyl-6-oxypyrimidine,



The Formation of the γ-Modification by Digestion of Guanidine Carbonate with Ethyl Benzoylacetate in Alcohol Solution.—Ten grams of ethyl benzoylacetate and 5.3 g. of guanidine carbonate were dissolved in 33 cc. of absolute alcohol and the solution digested on the steam bath for seven hours. A thick magma of the pyrimidine was obtained. This compound is practically insoluble in all the common organic solvents, but crystallized from hot dilute alcohol in slender prisms. These melted at 303° with effervescence. Mixtures of the α-modification and the β-modification with this γ-modification also melted at 303°. In other words, both forms underwent transformation to the γ-form on heating with this substance. This γ-modification dissolved immediately in dilute sodium hydroxide solution and was reprecipitated unaltered by addition of the required amount of hydrochloric acid.

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[1] Nitrogen by Kjeldahl method.

Calc. for $C_{10}H_9ON_3$: N, 22.46; found (Kjeldahl) N, 22.42, 22.48

This γ-modification dissolves in hydrochloric acid, giving the same salt as the α- and β-modifications. It contained one molecule of water of crystallization and crystallized in the same characteristic manner.

Calc. for $C_{10}H_{10}ON_3Cl.H_2O$: N, 17.39; Cl, 14.70; found N (Kjeldahl)· 17 27; Cl, 14.89.

Nitrogen determination in the free base, which was obtained by decomposing its hydrochloride with the required amount of alkali.

Calc. for $C_{10}H_9ON_3$: N, 22.46; found (Kjeldahl): N, 22.43.

The δ-Modification of 2-Amino-4-phenyl-6-oxypyrimidine.—In the preceding preparation of the γ-modification, the mother liquor obtained after filtration was heated in a pressure tube at 160–165° with 5 g. of guanidine carbonate (Warmington's method). Heating was continued for 6 hours. The solution was then evaporated to dryness and the residue warmed with a dilute solution of hydrochloric acid. On cooling a colorless salt separated. This was dissolved in water and alkali added, when a crystalline substance separated at once. This crystallized from alcohol in tables or plates, which melted at 279–280° with effervescence. It was soluble in water. A mixture of this product with the α-modification (m. p. 279–280°) melted at the same temperature. On the other hand, mixtures with the β- and γ-modifications melted at 303°. Notwithstanding the fact that this substance and the α-modification both melt at the same temperature, we have, however, obtained evidence that they are not identical. Consequently we have designated this substance as the δ-modification of 2-amino-4-phenyl-6-oxypyrimidine. The α-modification is characterized by the interesting fact that it can be transformed into the β-modification by boiling with alcohol. We have never observed such a transformation to take place in the case of this δ-modification. It was recovered unaltered after digestion in alcohol for 3 hours. In another experiment 1 g. of the pyrimidine was dissolved in about 100 cc. of absolute alcohol and the solution boiled for 7 hours. On cooling, the unaltered pyrimidine was obtained and melted at 279–280° with effervescence. A microphotograph of this δ-modification is represented by Fig. 4.

Calc. for $C_{10}H_9ON_3$ N, 22 46; found (Kjeldahl) N, 22 53, 22 53

This modification dissolves immediately in dilute sodium hydroxide solution and is reprecipitated unaltered by addition of acids. Analysis:

Calc for $C_{10}H_9ON_3$ N, 22 46; found N, 22 60.

When dissolved in hydrochloric acid it is transformed into the same salt as is obtained from the α-, β- and γ-modifications. This melts at 266° with effervescence and contains one molecule of water of crystallization. On decomposing the salt, by treatment in aqueous solution with the required amount of alkali, the γ-modification of the pyrimidine melting at 303° was obtained. This result was entirely unexpected, since the original base was obtained by decomposing its hydrochloride with alkali. Whether the presence of certain impurities retards the rearrangement, or whether the change is controlled by other conditions, such as temperature, and concentration of solution must be decided by further work. Analysis of hydrochloric acid salt:

Calc for $C_{10}H_{10}ON_3Cl.H_2O$ N, 17 39, found N, 17 59

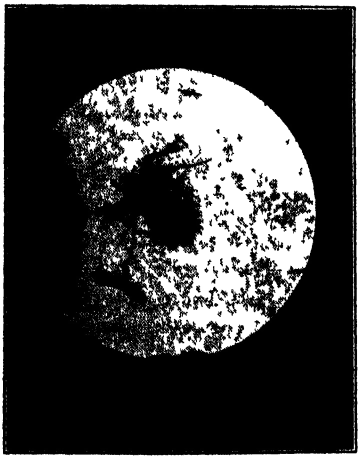


Fig. 3.—γ-Modification of phenylisocytosine, crystallized from alcohol. Magnified.

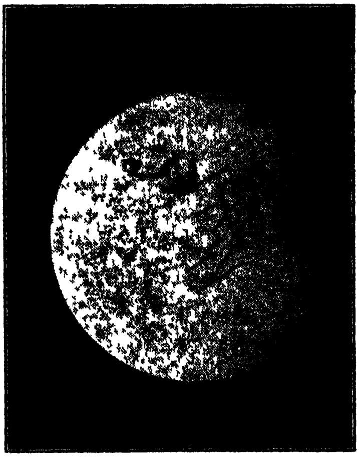


Fig 4 —δ-Modification of 4-phenyl-isocytosine crystallized from alcohol Magnified

Melting Points of the Mixtures of the Four Modifications of the Pyrimidines

279–280° α, δ; α + δ,

303°. . . β; γ, α + β, α + γ; β + γ, β + δ; γ + δ

All samples melt with effervescence.

New Haven, Conn

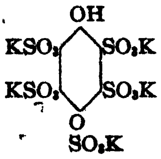
[Contributions from the Chemical Laboratory of Harvard University.]

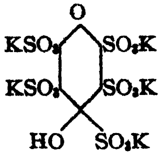
THE CONSTITUTION OF THIOCHRONIC ACID.[1]

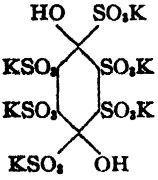
By C. Loring Jackson and S. A. Beggs

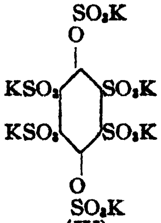
Received March 28, 1914

Potassium thiochronate was first prepared by the action of alkaline sulfites on chloroanil by Hesse,[2] and later studied by Grieff[3] and still more fully by Graebe,[4] who assigned to it Formula I, which has been universally adopted, although to make it agree with the analyses it is necessary to assume that this salt retains a molecule of water of crystallization even at 160°.


(I)


(II)


(III)


(IV)

Our attention was called to thiochronic acid by encountering it in the course of a research on the action of alkaline sulfites on tetrabromo-*o*-quinone,[5] and we were struck by the fact that Graebe's formula (I) does not explain several of the properties of the acid, thus:

(*a*) It is yellow, but there is no structure, in Formula I, which would account for this yellow color, for sulfonic acids, hydroquinones, and phenol sulfuric esters are all colorless.

(*b*) Baumann[6] has prepared many of the phenol sulfuric esters by the action of potassium pyrosulfate on the potassium salt of the phenol, and has found that, while easily decomposed by acids, the phenol sulfuric ester is very stable toward alkalies, since it can be boiled with a strong solution of potassium hydroxide without decomposition, and decomposes only slowly, even when heated with it in a sealed tube at 150°. The thiochronate therefore can hardly be a phenol sulfuric ester, because it is easily decomposed by potassium hydroxide with only moderate heating.

(*c*) The product of this decomposition is the potassium salt of euthiochronic acid, ($C_6(OH)_2(SO_3H)_2O_2$) an undoubted quinone, the appearance of which would not be expected from Formula I. In fact Graebe, in order to explain this transformation, is obliged to assume that SO_3K, splits off from one of the atoms of oxygen and hydrogen from the other, giving acid potassium sulfite and leaving the quinone oxygens of the euthiochronate. While it must be admitted that such a reaction is not impossible, we have not succeeded in finding any similar case in the chemical literature, so that, if this explanation is adopted, it can be only as a strained hypothesis; and yet, this is the only way of explaining this action according to (I), since an experiment tried by us has excluded the more probable theory that the oxygen of the air entered into the reaction, converting into the quinone the potassium salt of the hydroquinone,

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Sydney Adams Beggs.

[2] *Ann.*, 114, 324 (1860).

[3] *Jahrb.*, 1863, p. 392.

[4] *Ann.*, 146, 40 (1868).

[5] The results of this research will appear in a later paper.

[6] *Ber.*, 11, 1913 (1878).

$$C_6(SO_3K)_4(OK)_2,$$

which would be the first product of the action of potassium hydroxide on a substance with this formula. We found, however, that the euthiochronate was obtained easily, when the potassium hydroxide acted on the thiochronate in an atmosphere of hydrogen.

(*d*) A fourth objection to Formula I is found in the very slight stability of Baumann's phenol sulfuric esters, when alkalies were not present. Thus the potassium salt of resorcinol monosulfuric ester, the nearest relation to (I), of which Baumann gives the properties, decomposed frequently when its solution stood at ordinary temperature; and the phenol compound was decomposed by moist air, or when the attempt was made to dry it by heat; while the thiochronate is stable under all these conditions. It should be remembered, however, that the behavior of the sulfuric ester group might, perhaps, be modified by the presence of so many sulfonic groups in the thiochronate, and this, to a certain extent, weakens the force of objections (*b*) and (*d*).

These objections to Graebe's formula (I) induced us to consider a second formula (II) for potassium thiochronate, which is formed from quinone tetrasulfonate, $C_6(SO_3K)_4O_2$, by the addition of a molecule of acid potassium sulfite to one of the carbonyl groups of the quinone instead of to both, as in Formula I. The four objections to Graebe's formula do not apply to (II).

(*a*) The yellow color is accounted for by the remaining quinone oxygen. (*b*) The easy decomposition by potassium hydroxide would be expected, for, although we know of no similar quinone derivatives, a substance with Formula II belongs in the same class as the addition compounds of acid potassium sulfite with ketones, or aldehydes, all of which, as is well known, are easily decomposed by alkaline hydroxides.

(*c*) Such decompositions yield the ketone, or aldehyde, just as thiochronic acid yields euthiochronic acid. The fact that such addition compounds of other quinones with acid potassium sulfite are not known may be due to the ease with which the quinone oxygen atoms are reduced by the sulfite; whereas the quinonetetrasulfonate, in our case, might well continue unreduced long enough for the addition to take place, in view of the difficulty with which hydroquinones are formed from quinones highly charged with negative radicals, like the euthiochronate or chloranilic acid. That the ring structure of the quinone would not prevent the addition of acid potassium sulfite is shown by the formation of addition compounds from cyclopentanone[1] and cyclohexanone.[2]

(*d*) In stability also, the thiochronate stands nearer to this class of compounds than to the phenolsulfuric esters.

The adoption of (II) necessitates the discussion of another set of reactions of the thiochronate. By the action of water at 130°–140°, or heating with hydrochloric acid, or by treatment with reducing agents the thiochronate is converted into the potassium salt of hydroquinonedisulfonic acid, $C_6H_2(SO_3K)_2(OH)_2$, and at first sight this formation of a hydroquinone seems to agree better with (I) than with (II); but this is only apparent, since in all these experiments a reducing agent is present, and this would convert the quinone, formed at first according to (II), into the hydroquinone, which is the final product.

The arguments given above seemed to us to justify the adoption of (II) instead of (I), but, when we had arrived at this point, we were so fortunate as to stumble on new experimental evidence so convincing that it amounts to a proof of the correctness of (II). In the hope of determining the constitution of euthiochronic acid, for use in the research on *o*-quinonesulfonic acids already alluded to, we treated dibromodiphenoxyquinone with acid potassium sulfite. The principal product was potassium thiochronate, so that the experiment threw no light on the structure of euthiochronic acid, but in addition to this we obtained a small quantity of a white salt containing $(SO_3K)_6$, which would be represented by Formula III, if (II) is adopted for the thiochronate. It is formed, therefore, by an addition of acid potassium sulfite to the second quinone carbonyl in the same way that (II) was formed by addition to the first, and such a compound would be expected in this case. On the other hand, we cannot bring this substance into harmony with (I), since according to that formula both the quinone carbonyls have taken part in the formation of the thiochronate, and this has left no way in which acid potassium sulfite can cause the introduction of a sixth SO_3K. And it is no better for Formula I, if we suppose that a compound with $(SO_3K)_6$ could be formed from it in some unexplained way, for this could have only Formula IV. This is inadmissible, because such a compound must give hydroeuthiochronic acid by the action of potassium hydroxide in an atmosphere of hydrogen, that is, under these conditions it could not produce the quinone euthiochronic acid, which was actually obtained by us in an experiment, and is the natural product, if our acid had the constitution represented by (III). The white color is also explained by this formula, as the last of the chromophoric groups has been modified. We propose for our new compound the name hexachronic acid.

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[1] Claisen, *Ber*, 8, 1257 (1875); Pinner, *Ibid*, 15, 594 (1882).

[2] Baeyer, *Ann*, 278, 101 (1894).

To sum up our arguments, Formula II explains, while (I) does not, the yellow color, the stability especially toward alkalies, the formation of euthiochronic acid and of hexachronic acid.

Other unsuccessful attempts to determine the constitution of euthiochronic acid led to an unexpected result, for, when bromoanilic acid was treated with acid potassium sulfite, both the atoms of bromine were replaced by hydrogen, giving 1,2,4,5-tetrahydroxybenzene. We have been able to find only a few other cases in which bromine has been replaced by hydrogen in aromatic compounds under the influence of sulfites, or sulfurous acid. Stenhouse obtained a partial conversion of bromoanil into tribromohydroquinone, when sulfur dioxide acted on it in boiling water;[1] the formation of dianilino-*p*-quinoneanil from dianilinobromoquinoneanil by an ethereal solution of sulfur dioxide[2] has been observed; likewise the formation of the corresponding dibromo compounds from tribromodinitro- and tribromotrinitrobenzene by alcoholic sodium sulfite.[3]

The marked difference between the action of the acid sulfite on dibromodiphenoxyquinone, giving thiochronate and hexachronate, and on dibromodihydroxyquinone (bromoanilic acid), giving 1,2,4,5-tetrahydroxybenzene, is probably to be ascribed to the presence of free sulfurous acid in the latter case. Accordingly we tried to exclude this by using potassium bromoanilate instead of bromoanilic acid. To our surprise, each addition of the salt to the acid potassium sulfite solution was accompanied by a brisk effervescence of sulfur dioxide, so that the conditions were the same as in the previous experiment, and no light was thrown on the subject. The unexpected evolution of sulfur dioxide is undoubtedly due to the fact that the $C_6Br_2(OK)_2(OH)_2$ formed at first from the bromoanilate is acid enough to decompose the sulfite. That the replacement of the bromine was not due to nascent sulfur dioxide was shown by treating potassium bromoanilate with free sulfur dioxide, when the bromine was eliminated with no more trouble than in the preceding experiment. Bromoanilic acid, on the other hand, when treated with sulfurous acid, loses bromine much less easily than the bromoanilate. It is to be observed that the bromine atoms in bromoanilic acid stand between two atoms of oxygen, and therefore in the position most favorable to their replacement by hydrogen, as has been shown by numerous experiments tried in this laboratory. Whether the loosening of the bromine is due to two hydroxyls, or to a hydroxyl and a quinone oxygen, that is, whether the quinone is reduced before or after the removal of the bromine cannot be decided on our present data.

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[1] *Ann. Supp.*, **8**, 20 (1872). Similar work with chloroanil, *Ibid., Supp.* **6**, 214 (1868).

[2] Jackson and Porter, *Am. Chem. J.*, **30**, 518 (1903).

[3] Jackson and Earle, *Ibid.*, **26**, 46 (1901).

Tin and hydrochloric acid also convert bromoanilic acid into 1,2,4,5-tetrahydroxybenzene. The two atoms of oxygen therefore produce the same loosening effect on the bromine that has been observed previously with nitro or amino groups alone, or nitro in conjunction with hydroxyl groups.[1]

We found that the 1,2,4,5-tetracetoxybenzene melted at 226–227° (uncorr.) instead of at 217°, as given by Nietzke and Schmidt.[2] The 1,2,4,5-tetrahydroxybenzene yielded a well crystallized black tetrahydroxyquinhydrone, when its solution was exposed to the air after acidification with hydrochloric acid.

Experimental.

Preparation of Potassium Thiochronate.—The following method for preparing thiochronic acid gives a better yield than those previously described:[3] Ten grams of chloroanil were heated with a solution of 50 g. of dipotassium sulfite (prepared just before the experiment) in 100 cc. of water. After boiling for 20 minutes the liquid was allowed to cool and the yellow solid washed with cold water and recrystallized from boiling water. The yield was about 9 g., that is, 32% of the theoretical.

Action of Potassium Hydroxide on Potassium Thiochronate in an Atmosphere of Hydrogen.—A slow stream of hydrogen was passed through two Erlenmeyer flasks, escaping from the last through a Bunsen valve to prevent the entrance of air. The first of these flasks contained the solution of potassium hydroxide, the second 10 g. of potassium thiochronate in 50 cc. of water. After the apparatus was full of hydrogen, the contents of each flask were boiled, until all the dissolved air had been expelled, when, by tipping the first flask, the potassium hydroxide was forced over by the hydrogen into the second. The solution turned very dark at first, and then became light yellow, and deposited a yellow solid, which was filtered out after the liquid had cooled in the atmosphere of hydrogen. The yellow solid was recognized as the tetrapotassium salt of euthiochronic acid by the addition of a drop of dilute hydrochloric acid, which converted it into the very characteristic vivid red tripotassium euthiochronate, which was again changed to the yellow tetrapotassium salt by a few drops of potassium hydroxide.

[1] Schliepper, *Ber.*, 25, 553 (1892); 26, 2465 (1893); Hübner, Petermann, *Ann.*, 149, 135 (1869); Bässmann, *Ibid.*, 191, 244 (1878); Zincke, *Ber.*, 5, 792 (1872); Jackson, Calvert, *Am. Chem. J.*, 18, 467 (1896).

[2] *Ber.*, 21, 2378 (1888).

[3] Hesse, *Ann.*, 114, 324 (1860); Graebe, *Ibid.*, 146, 40 (1868).

Action of Acid Potassium Sulfite on Dibromodiphenoxyquinone.—One gram of dibromodiphenoxyquinone was heated on the steam bath in an Erlenmeyer flask with a solution of 5 g. of acid potassium sulfite in 10 cc. of water, but, as there was no action, enough potassium hydroxide was added to start a reaction. When the solution had turned brown, it was filtered, and as it cooled it deposited yellow crystals. Seven grams of the dibromodiphenoxyquinone yielded about 6.5 g. of this crude product, which, on crystallization from water, was found to consist principally of a yellow compound mixed with a small amount of a white one. The yellow substance, which contained no bromine, was purified by six crystallizations from water.

Subst. 0.3130, 0.3354; loss at 120° 0.0227, 0.0241.

Calc. for $C_6(SO_3K)_5O_2H.4H_2O$ ($3H_2O$ lost), 7.00; found: H_2O, 7.25, 7.19.

Subst. 0 2891, 0.2854, K_2SO_4 0.1772, 0.1753.

Calc. for $C_6(SO_3K)_5O_2H.H_2O$, K, 27.28; found: K, 27.51, 27.57.

These analyses show that it is potassium thiochronate, which, according to Graebe, contains 4 molecules of water, only 3 of which are given off at 120°; and this conclusion was confirmed by the fact that our substance showed the two characteristic reactions of the thiochronate. An aqueous solution gave a white precipitate with barium chloride, which melted when the supernatant liquid was boiled, and when treated with potassium hydroxide the boiling solution was converted into potassium euthiochronate, recognized by the yellow color of its tetrapotassium salt, which crystallized out on cooling, and the red tripotassium salt obtained when a boiling solution of the yellow salt was treated with a few drops of dilute hydrochloric acid.[1]

Potassium Hexachronate, $C_6(SO_3K)_4((OH)(SO_3K))_2.3H_2O$.—The white part of the product from the action of acid potassium sulfite on dibromodiphenoxyquinone was purified by crystallization from water and air dried. It contained no bromine.

Subst. 0.3035, lost at 120° 0.0200; calc. for $C_6(SO_3K)_6O_2.3H_2O$: H_2O, 6.19; found: 6.59.

Subst. dried at 120° 0.2834, 0.1602; K_2SO_4, 0.1824; $BaSO_4$, 0.2741; Calc. for $C_6(SO_3K)_6O_2$, K, 28.65; S, 23.45; found: K, 29.89; S, 23.51.

We propose for this substance the name hexachronic acid.

Properties of Potassium Hexachronate.—White crystals, which lose crystal water at 120°. Very slightly soluble in cold water, more soluble in hot; soluble in alcohol. Strong hydrochloric acid, or nitric acid, produces no visible effect; strong sulfuric acid dissolves it with evolution of sulfur dioxide.

A little of the salt was dissolved in hot water and two drops of a solution of potassium hydroxide were added, which turned the liquid yellow, and on cooling yellow crystals were deposited. These were washed with a little cold water, dissolved in hot water, and treated with a drop of dilute hydrochloric acid, when the solution turned red, and on cooling vivid red crystals separated. There can be no doubt, therefore, that this product was potassium euthiochronate. The same result was obtained when the hexachronate was treated with potassium hydroxide in an atmosphere of hydrogen. The yield of hexachronate is very small, most of the dibromodiphenoxyquinone being converted into thiochronate. For this reason we were unable to study other hexachronates.

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[1] Graebe, *Ann.*, 146, 40 (1868); Hesse, *Ibid.*, 114, 313 (1860).

In an attempt to determine the constitution of euthiochronic acid the 2,5-dichloro-3,6-dibromoquinone was treated with acid potassium sulfite, and a product obtained which seemed to be a mixture of dibromohydroquinonedisulfonate and the corresponding dichlorocompound, as the percentage of potassium fell between those required by the former compound and the chlorobromohydroquinonedisulfonate. As we found the composition of the product was not changed by 5 crystallizations, we decided it was an isomorphous mixture, and abandoned that line of work.

Action of Acid Potassium Sulfite on Bromoanilic Acid.—This was another of our unsuccessful attempts to determine the constitution of euthiochronic acid. A solution of acid potassium sulfite, containing 5 g. in 10 cc. of water, was warmed in an Erlenmeyer flask on the steam bath, and 1 g. of bromoanilic acid was added in small portions at a time, the solution being kept just warm enough to dissolve the bromoanilic acid at once. Each addition produced an effervescence of sulfur dioxide, and a white solid began to separate, after three-quarters of the acid had been added. At the end of the experiment the liquid was allowed to cool, when the white insoluble product was deposited in quantity, and it was found to contain potassium, but neither bromine nor sulfur. On attempting to crystallize it from water, in which alone it was soluble, it oxidized so rapidly that there was no hope of purifying it in this way. Accordingly, it was dissolved in hot water and treated with strong hydrochloric acid in excess, when, on cooling, yellow crystals were deposited. This behavior made it probable that the colorless crystals were the potassium salt of 1,2,4,5-tetrahydroxybenzene, and the yellow crystals 2,5-dioxyquinone. We proceeded as follows to test this supposition: The yellow crystals were covered with strong hydrochloric acid and heated with tin on the steam bath, till a colorless solution was obtained, which, after the excess of tin had been filtered out gave, on cooling, white crystals free from potassium. As the 1,2,4,5-tetrahydroxybenzene has no sharp melting point and the dioxyquinone does not melt, we converted our product at once into the acet compound by warming 2 g. of it with an excess of acetic anhydride and 2 g. of fused sodium acetate in an Erlenmeyer flask on the steam bath. After 20 minutes 50 cc. of water were added, which threw down the acet compound in practically quantitative yield. It was purified by crystallization from glacial acetic acid, until it showed the constant melting point 226–227° (uncorr.). This was a great surprise to us, as Nietzki and Schmidt[1] found that the 1,2,4,5-tetracetoxybenzene melted at 217°. Since isomers are out of the question, we are of the opinion that the melting point given by Nietzki and Schmidt is wrong, because the following analysis shows that our substance is the tetracetoxybenzene:

Subst. 0.1015; CO_2, 0.2012, H_2O, 0.0444; Calc. for $C_6H_2(OC_2H_3O)_4$: C, 54.20; H, 4.52; found: C, 54.06; H, 4.86.

The same compound was obtained when bromoanilic acid was heated with tin and hydrochloric acid, until the solution became colorless. Enough water was then added to dissolve the white solid with the aid of heat and the solution was filtered hot. On cooling, white crystals separated, which, after drying on a porous plate, were heated with acetic anhydride for half an hour. The product was precipitated with hot water, and after one crystallization from glacial acetic acid it melted at 224–225°. This, with the fact that it contained no bromine, was enough to show that it was the 1,2,4,5-tetracetoxybenzene.

If a solution of the potassium 1,2,4,5-tetrahydroxybenzene was acidified with strong hydrochloric acid and exposed to the air for two days, clusters of small, black, slender plates, terminated by a single plane at an oblique angle and showing a yellow reflex, were deposited, which we supposed were the quinhydrone. As an analysis would show nothing, we tested our hypothesis as follows: A mixture of the tetrahydroxybenzene and dioxyquinone with a little water was heated on the steam bath, when, on cooling, the same black substance crystallized out. Upon heating some of the original black crystals in matched watch glasses a yellow sublimate of dioxyquinone was obtained. There can be no doubt, therefore, that our new substance is a tetrahydroxyquinhydrone.

Action of Acid Potassium Sulfite on Potassium Bromoanilate.—The potassium salt was made by adding potassium hydroxide in excess to bromoanilic acid suspended in warmed water. The salt went entirely into solution at one stage of the experiment, and was then precipitated by an excess of the hydroxide. The solid was sucked out on the filter pump and washed with a little alcohol; the preparation, therefore, could contain no free acid. The acid potassium sulfite was freshly prepared, and warmed, and treated with potassium hydroxide, drop by drop, until the odor of sulfur dioxide had disappeared. To such a solution, prepared from 5 g. of potassium hydroxide in 10 cc. of water, the bromoanilate from 1 g. of acid was added in small portions at a time, while the solution was gently warmed. Each addition gave a vigorous effervescence of sulfur dioxide and the product was white and crystalline. To this excess of strong hydrochloric acid was added and the mixture exposed to the air, when in two days a fine, black, crystalline precipitate of the quinhydrone was formed, showing that the original product was the 1,2,4,5-tetrahydroxybenzene.

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[1] *Ber.*, 21, 2378 (1888).

A stream of sulfur dioxide was passed into water containing potassium bromoanilate prepared as above. A red precipitate looking like bromoanilic acid was at first formed, but on longer action a colorless product was obtained, which, on exposure to the air, gave black crystals of a quinhydrone, while the aqueous liquid gave a strong test for a bromide.

Bromoanilic acid warmed with water and exposed to a stream of sulfur dioxide lost bromine, as was shown by a test for hydrobromic acid in the filtrate, but this reduction took place more slowly than in the case of the bromoanilate, and was not complete at the end of the reaction.

CAMBRIDGE, MASS

THE PREPARATION OF DIMETHYLGLYOXIME WITHOUT THE USE OF HYDROXYLAMINE.

BY J. M. JOHLIN, JR.

Received April 6, 1914.

Schramm[1] has made the observation that isonitrosomethylacetone—the monoxime of diacetyl—dissociates, when treated with hydrochloric acid, into hydroxylamine, acetic acid and other unidentified products, yielding upon evaporation 81% of the theoretical amount of hydroxylamine hydrochloride. He also observed the formation of minute quantities of ethylmethylacetoximic acid—the dioxime of diacetyl—by the interaction of the liberated hydroxylamine with the still undissociated monoxime. He prepared larger amounts of the dioxime from the monoxime with hydroxylamine.

v. Pechmann[2] has since shown that, in part, the dissociation products of the isonitrosoketone are hydroxylamine and diacetyl. Diels and Jost[3] adapted this property as the basis of a method for the preparation of the diketone. Since dimethylglyoxime has been given. added importance through its employment in the qualitative and quantitative determination of nickel, Gandarin[4] has more recently pointed out that it can be more economically prepared by adding hydroxylamine to the sodium salt of the monoxime without isolating the latter as the acid monoxime.

Operating according to the modified method of Diels and Stephan[5] for the preparation of diacetyl, 850 cc. of methylethylketone are mixed with 30 cc. of concentrated hydrochloric acid and one liter of isoamylnitrite slowly added at 50°. The resulting mixture is shaken with caustic soda, the alkaline layer acidified with 25% sulfuric acid, and, upon the addition of concentrated sulfuric acid, distilled with steam for the recovery of the liberated diacetyl.

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[1] *Ber.*, 16, 180 (1883).

[2] *Ibid.*, 20, 3213 (1887).

[3] *Ibid.*, 35, 3290 (1902).

[4] *J. prakt. Chem.*, 77, 414 (1908).

[5] *Ber.*, 40, 4337 (1907).

Recently, while operating according to this method of preparing the diketone, it was noted that if the reaction products are allowed to stand two hours before shaking with caustic soda, a mixture of minute quantities of ammonium chloride and dimethylglyoxime will separate from them. It was further observed that if, after shaking with caustic soda and acidifying with 25% sulfuric acid, the mixture is allowed to stand 24-36 hours large amounts of dimethylglyoxime will have crystallized out at the bottom of the flask, while the oily or solidified layer which rose to the surface of the liquid upon acidification will have almost disappeared. The mother liquor can be further treated for the recovery of diacetyl according to the prescribed method, while the crystalline dimethylglyoxime can be purified by boiling with animal charcoal and a large amount of water. Filtering by means of a steam funnel and cooling will result in a very pure product without considerable loss due to the recrystallization. 850 cc. of commercial methyl ethyl ketone will yield 50-60 g. of the pure glyoxime as a by-product.

Tschugaeff[1] has mentioned some of the properties of the nickel salt of dimethylglyoxime. It was nevertheless considered of interest to further investigate some of these properties, as well as to study the conditions under which the acid dioxime will form the monoxime without the additional use of hydroxylamine, and to study some of the properties of the dioxime itself.

Thirty-five grams of pure dimethylglyoxime were steam-distilled in the presence of 200 cc. of 25% sulfuric acid freshly prepared from concentrated. The otherwise insoluble dioxime dissolved in the hot mixture, which, due to the fact that diacetyl was set free, became colored a greenish yellow. The diketone thus liberated was carried over in the course of the distillation and the liquid in the flask as well as the space above it became colorless. The steam-distillation was continued until the volume of distillate amounted to 500 cc. This distillate was saturated with salt and the mixture again steam-distilled. It was noted that after all the diacetyl had apparently been distilled over there still remained on the surface of the liquid in the flask a colorless oil which solidified upon cooling, while the condenser had become clogged with a crystalline substance which proved to be the monoxime of diacetyl. The distillation was continued and additional amounts of the monoxime recovered.

The first part of the distillate was again steam-distilled, and the diketone which was recovered dried over calcium chloride. Subjected to a distillation it was found to boil within the range of 60–90°. It is evident, then, that pure dimethylglyoxime upon its dissociation with sulfuric acid yields other products besides diacetyl. The yield amounted to 10% of the theoretical. Because of the small amount of the oil obtained, the nature of its complexity has not been investigated. Since the monoxime of diacetyl is readily soluble in water, no doubt the larger part of the original 35 g. of dioxime used remained behind in the form of the monoxime when the steam-distillation in the presence of sulfuric acid was carried on, while a lesser part was carried over as diacetyl or its monoxime during the distillation.

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[1] *Z. anorg. Chem.*, 46, 145 (1905).

The monoxime which was recovered as mentioned was dried upon a porous plate and found to melt sharply at 76°. It possesses the sweet pungent taste of diacetyl itself and when exposed to the air in an open dish will volatilize completely at room temperature. Its dissociating properties were further studied.

A small portion of the monoxime was dissolved in water, a few drops of dilute hydrochloric acid added and to the mixture immediately added a few drops of ammoniacal nickel solution. An immediate heavy precipitation of the nickel salt of dimethylglyoxime resulted, indicating the readiness with which the monoxime will dissociate into hydroxylamine and diacetyl which products recombine in neutral or alkaline solution to form the less soluble dioxime.

A second portion similarly treated with dilute sulfuric acid was found to dissociate less readily. The dissociation was hastened by boiling, whereupon an immediate precipitation of the nickel salt was obtained when a few drops of an ammoniacal nickel solution were added to the mixture.

A third portion was allowed to stand with dilute acetic acid for two weeks. Tests made with ammoniacal nickel solution at repeated intervals showed that none of the monoxime had dissociated.

A fourth portion was dissolved in water, a few drops of ammoniacal nickel solution added and the mixture allowed to stand for two weeks. The mixture gradually assumed a slight yellow color but there were no indications of the formation of a precipitate, even upon boiling.

Further indications of the dissociating powers of these acids are exhibited by their action upon the nickel salt of dimethylglyoxime. When this salt is treated even with dilute hydrochloric acid the insoluble acid dioxime is at once liberated; upon standing for an hour the dioxime will also completely dissolve in the hydrochloric acid.

Similar treatment with dilute sulfuric acid will set free the acid dioxime from the nickel salt less readily, and, even when boiled, the action goes on at a much slower rate than when dilute hydrochloric acid is used.

Tschugaeff observes that sodium hydroxide is without effect upon the nickel salt and that even boiling glacial acetic acid causes but little decomposition. It is to be observed that when the nickel salt is treated with a boiling solution of even dilute caustic soda complete decomposition will be effected. A 25% acetic acid solution will also slowly decompose the nickel salt, which will again reprecipitate when ammonium hydroxide is added.

From the properties which have been exhibited by dimethylglyoxime and isonitrosoacetone, it appears that treatment with sulfuric acid, if it is not too concentrated, will afford the most satisfactory conditions under which the monoxime will dissociate and the less soluble dioxime precipitate as a result of this dissociation.

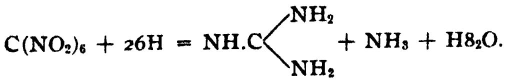
SYRACUSE UNIVERSITY.

LIMITS OF THE ATTACHMENT OF AMINO GROUPS TO A SINGLE CARBON ATOM; ATTEMPTS TO PREPARE TETRAMINO METHANE.

By JITENDRA NATH RAKSHIT

Received January 3, 1914.

All attempts to prepare compounds containing more than two amino groups attached to a single carbon atom have resulted in combinations of nitrogen with the carbon in some other form, such as the cyanogen or imido group. Ammonia and chloroform[1] at red heat give hydrocyanic acid. Aniline and chloroform[2] give formamidine, Ph.NH.CH : NPh. Chloropicrin[3] or carbon tetrabromide[4] and ammonia give guanidine. Carbon tetrachloride also yields triphenyl guanidine with aniline. Guanidine contains the largest number of nitrogen atoms which it has hitherto been found possible to combine with a single carbon atom. It was thought possible that the reduction of tetranitro methane might give tetramino methane, but on carrying out the experiment guanidine and ammonia were obtained.



$$C(NO_2)_6 + 26H = NH.C\begin{cases} NH_2 \\ NH_2 \end{cases} + NH_3 + H8_2O.$$

Experimental.

Tetranitro methane was prepared according to Chattaway's[5] method. Two hundred grams of zinc were kept immersed in a dilute solution of nickel sulfate over night. The nickel coated zinc was washed and transferred to an Erlenmeyer flask and 5 cc. of tetranitro methane and 20 cc.

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[1] Andre, *Compt. rend.*, 102, 553.

[2] Hofmann, *Proc. Roy. Soc.*, 9, 229.

[3] Hofmann, *J. Chem. Soc.*, 19, 251.

[4] Bolas and Groves, *Ibid.*, 24, 782.

[5] *J. Chem. Soc.*, 97, 2099 (1910).

water were added. From a buret, 10% hydrochloric acid was added in 4 cc. portions with constant shaking, the temperature being maintained at 20–25°. When all oily drops had disappeared, further 20 cc. of dilute acid was added and the mixture was left over night in a cool place. The solution was then decanted and the zinc was precipitated as carbonate with soda. The filtrate from the zinc carbonate was evaporated on the water bath after acidulating with dilute hydrochloric acid. The residue obtained was powdered on a mortar and extracted with absolute alcohol. The alcoholic extract was evaporated on the water bath and the residue was again extracted with a mixture of equal volumes of absolute alcohol and ether, and the extract evaporated. The substance thus obtained was free from ammonium and sodium chlorides. It was a white crystalline deliquescent substance. The fact that guanidine hydrochloride, like most other amine hydrochlorides, is soluble in alcohol or in a mixture of alcohol and ether, and the insolubility of sodium and ammonium chlorides, rendered its separation simple.

0.3161 g. gave 0.4690 g. AgCl; calc. for $NHC(NH_2)_2HCl$: Cl = 36.84; found: 36.69.
0.1050 g. chloroplatinate gave 0.0392 g. Pt; calc. for $[NHC(NH_2)_2HCl]_2PtCl_4$: Pt = 37.00; found: 37.38.

The residue from the first extract was dissolved in a small quantity of water and distilled with caustic soda. The distillate was found to be ammonia pure and simple.

This reduction was also carried through with tin and hydrochloric acid, with subsequent removal of the tin as sulfide. In this case the product obtained was a mixture of ammonium chloride and guanidine hydrochloride.

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[CONTRIBUTIONS OF THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,
No. 234.]

THE ADDITION COMPOUNDS OF DIMETHYLPYRONE WITH ORGANIC ACIDS.[1]

BY JAMES KENDALL.

Received April 20, 1914.

The addition products of dimethylpyrone with acids are of special interest in view of their connection with the oxonium theory of Collie and Tickle.[2] The hypothesis that oxygen may function as a quadrivalent atom was first brought into prominence by a study of these compounds, the action being regarded as proceeding according to the equation:

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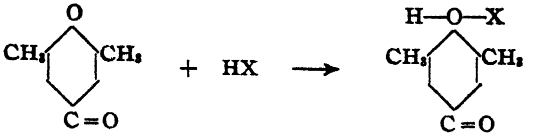
[1] Presented at the Cincinnati meeting of the American Chemical Society, April 9, 1914.

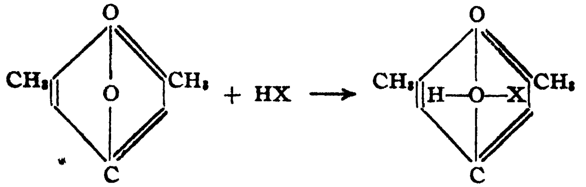
[2] *J. Chem. Soc.*, 75, 710 (1899).



(I)

It is assumed in this equation (no reason being given) that addition takes place by means of the oxygen in the ring. Subsequent investigators have regarded the "carbonyl" oxygen in the side-chain as active, the addition products formed being considered as analogous with those given by aldehydes and ketones with acids. Since, however, ethers also react with acids to form addition compounds, it is evident that either assumption may be correct.

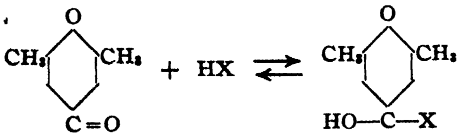
Collie's later views regarding the structural formulae of dimethylpyrone and its salts[1] lead to the following equation:



(II)

Here dimethylpyrone itself is considered as containing a quadrivalent oxygen atom, and, in the addition compound, both oxygen atoms are regarded as quadrivalent. These assumptions are supported by the work of Homfray on molecular refraction,[2] and also by the spectroscopic measurements of Baly.[3] On the other hand, Willstätter and Pummerer[4] have advanced reasons against the assumption of quadrivalent oxygen in dimethylpyrone itself.

It does not seem to be regarded as definitely established, indeed, that oxygen functions as a quadrivalent atom at all in the above reaction. Werner[5] has explained the constitution of the addition products with the help of his theory of subsidiary bonds. Gomberg and Cone[6] have denied the formation of an oxonium salt entirely, and consider the action as taking place according to the scheme:



(III)

A great deal of evidence in favor of this view is adduced.

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[1] *J. Chem. Soc.*, 85, 973 (1904).

[2] *Ibid.*, 87, 1443 (1905).

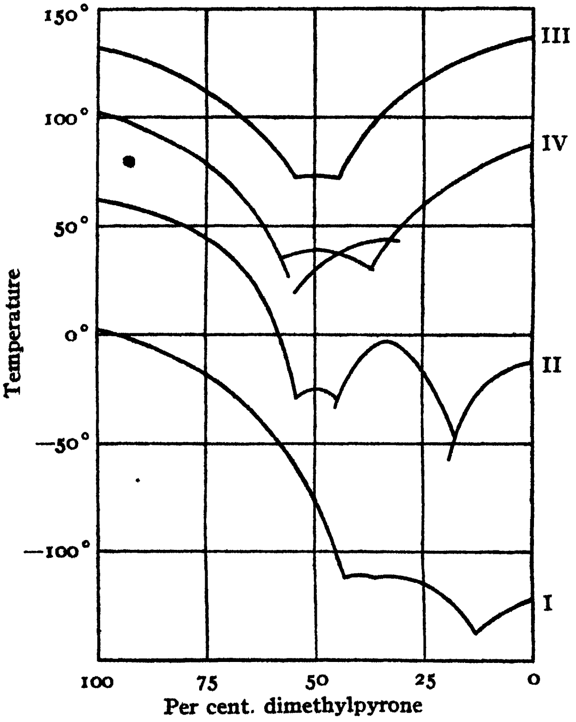
[3] *Ibid.*, 96, 144 (1909).

[4] *Ber.*, 37, 3740 (1904); 38, 1461 (1905).

[5] *Ann.*, 322, 296 (1902).

[6] *Ibid.*, 376, 217 (1910).

The most cogent arguments against the above conception of the reaction are to be obtained from the work of McIntosh,[1] who has investigated these addition compounds by physico-chemical methods. Dimethylpyrone, dissolved in liquid hydrogen bromide or hydrogen chloride, gives a conducting solution. Dimethylpyrone itself is not an electrolyte, consequently, combination with the solvent must have taken place. The compound cannot be represented according to (III) above, since an addition product of such nature (with a halogen and hydroxyl attached to the carbon) should not be ionized. Furthermore, the addition products isolated were not necessarily equimolecular; for example, with HBr the three compounds $C_7H_8O_2$, HBr; $C_7H_8O_2$, 2HBr; $C_7H_8O_2$, 4HBr were obtained. These latter compounds can be represented satisfactorily only on the assumption that both oxygen atoms in dimethylpyrone are unsaturated, and may function as quadrivalent. In the most complex salt, indeed, oxygen is regarded by McIntosh as hexavalent.



I. Formic acid. Add 130° to temperature scale.
II. Trichloracetic acid. Add 70° to temperature scale.
III. Cinnamic acid. Temperature scale correct.
IV. Mandelic acid. Add 30° to temperature scale.

Fig. 1.

The work of Maass and McIntosh on the addition compounds of ethers and alcohols with the halogen acids[2] is also of importance, since in these substances there is no carbonyl oxygen present, and the action cannot be represented according to (III) above. In these investigations the existence of compounds is shown by an examination of the freezing point curve of the two-component system, ether (or alcohol)–acid. The experimental difficulties connected with the work (due to the very low temperatures of fusion of the substances studied) have caused the important point that the above is a *general method* for the examination of organic addition reactions, to escape observation.

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[1] This Journal, 32, 542 (1910).

[2] *Ibid.*, 34, 1273 (1912).

In the following pages this freezing point method is applied to the study of the addition compounds formed by dimethylpyrone with organic acids. The addition products of dimethylpyrone itself have been little investigated, in spite of the large amount of speculation on the nature of oxonium compounds. It was consequently hoped that the results obtained by a systematic examination would throw some light on the problems involved in the above discussion.

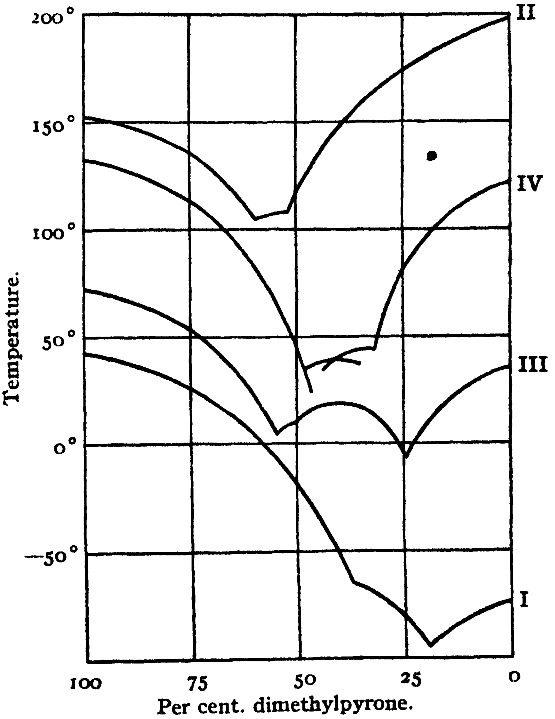
The following compounds of dimethylpyrone with organic acids have already been described:

(*a*) Collie and Tickle,[1] oxalate, tartrate, salicylate, chloroacetate, picrate. (All attempts to isolate the acetate were unsuccessful.)

(*b*) Plotnikow:[2] trichloroacetate, tribromoacetate.

The present investigation comprises more than thirty organic substances of acidic nature (monobasic, aliphatic and aromatic acids, and phenols).

The theoretical basis of the method may be briefly outlined. If, to a pure substance, A, we add a second, B, the freezing point of A is lowered; similarly, addition of A lowers the freezing point of B. Plotting temperature against molecular concentration, we obtain two curves, which intersect at the eutectic point.



I. Acetic acid. Add 90° to temperature scale.
II. *p*-Toluic acid. Subtract 20° from temperature scale.
III. α-Naphthol. Add 60° to temperature scale
IV. β-Naphthol Temperature scale correct.

Fig. 2.

If, however, a compound A_xB_y is formed, this also acts as a pure substance, and its freezing point is lowered by addition of either A or B.

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[1] *Loc. cit.*

[2] *J. Russ. phys. chem. Ges.*, 36, 1088 (1904); 40, 64 (1908).

Hence the freezing point curve exhibits, in this case, a maximum, the position of the maximum on the axis of molecular concentration indicating the composition of the compound. A series of compounds is indicated by a series of maxima on the curve.

Now the action $xA + yB \longrightarrow A_xB_y$ is a reversible reaction, and the addition compound is always more or less dissociated into its two components. The maximum of the curve, therefore, is not sharp, but more or less "rounded-off." The flatness of the curve in the neighborhood of the maximum serves, indeed, as a measure of the degree of the dissociation.[1] This is important in the consideration of the relative dissociation of the various compounds described below.

In certain cases a compound is not stable at its maximum. Its composition must then be determined either from the curve, by extrapolation, or experimentally by analysis of the solid phase separating from the solution.

Experimental.

The ordinary Beckmann freezing point apparatus was employed. The outer bath (paraffin, water, ice—salt, or ether—carbon dioxide snow, according to the temperature required) was maintained at a temperature slightly below the freezing point of the mixture contained in the inner tube, and the latter slowly cooled, with constant stirring. In favorable cases the solid phase separated out after very slight supercooling, and the temperature rose rapidly to the true freezing point.[2] More frequently, however, considerable supercooling took place before crystallization began; it was then necessary to melt up again, preserving a small portion of the solid phase in the upper part of the tube, and repeat the experiment, seeding the liquid at intervals with crystals by means of the stirrer. In cases where crystallization was so sluggish that no rise of temperature on freezing could be obtained, the first sign of crystallization *in* the liquid under the above conditions was taken as indicating the freezing point. The temperature thus obtained could be confirmed by raising the temperature of the outer bath very slowly, and observing the disappearance of the solid phase.

The thermometers employed in the investigation were:

(*a*) a mercury thermometer, —10° to 110°, graduated in 1/10°.

(*b*) a mercury thermometer, 90° to 200°, graduated in 1/5°.

(*c*) an alcohol thermometer, 50° to —50°, which could be read to 1/5°.

The thermometers were standardized at the freezing point and boiling point of water by the usual methods, and at other temperatures by comparison with a standard thermometer. A temperature-correction curve for exposed stem was also obtained, and the necessary correction applied to every reading taken.[1] The constancy of the thermometers during the course of the investigation was examined by careful repetition of the above tests at intervals. The temperatures given in the tables below may be taken as having the following degree of accuracy:

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[1] Kremann, *Monats.*, 25, 1222 (1904).

[2] This method is obviously inapplicable on steep portions of the curve, where the freezing point of the mixture changes rapidly with change of composition. Here also it was necessary to employ the more tedious method of observing appearance or disappearance of solid phase.

(*a*) between 200° and 100°: 0.2–0.5°.
(*b*) between 100° and 0°: 0.1–0.2°.
(*c*) between 0° and —50°: 0.2–0.5°.

The difficulty of measurement varied very considerably with the system under examination. In some systems, especially at low temperatures, a glassy mass was obtained in which it was extremely difficult to observe appearance or disappearance of crystals.

The composition of the mixtures examined is expressed throughout, in the tables below, in molecular percentages of the components. A known weight of one component was taken, and successive quantities of the second introduced into the apparatus through the side tube in the form of compressed tablets. Liquids were added by means of the Lunge pipet. Deliquescent substances were introduced from a weighing bottle after careful drying in a desiccator, and contact with the outer air was made as short as possible.

Dimethylpyrone melts at 132.1°, but begins to sublime below 80°, and above 100° the amount of sublimation in a short time is appreciable.[2] Hence the freezing points of mixtures containing, in general, more than 70% dimethylpyrone could not be determined by the ordinary Beckmann method. The following method was adopted, and, by it, results of approximate but sufficient accuracy were obtained. A weighed amount of dimethylpyrone (about 0.1 g.) and a smaller amount (unweighed) of acid were introduced into a narrow glass tube, the tube sealed, and attached to the thermometer. Thermometer and tube were now immersed together in sulfuric acid, contained in the inner freezing point tube, and the outer bath (paraffin) heated until the contents of the tube melted. It was usually necessary to repeat fusion several times before a homogeneous mixture was obtained. The freezing point could be determined, within 0.5° to 1.0°, by observing disappearance of crystals with a slowly rising temperature. Finally, the composition of the mixture was determined by cooling the tube, dissolving the contents in water, and titrating the acid against a standardized solution of barium hydroxide.[3]

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[1] This correction varied from 0.1° at 50° to 1.6° at 180°.

[2] This does not apply to mixtures containing only a small percentage of dimethylpyrone. Such mixtures could be investigated up to 150° without appreciable sublimation.

[3] Where the acid was insoluble in water, or could not be titrated accurately against barium hydroxide, larger amounts were taken, and the acid used directly weighed.

The above procedure was necessary, in a few systems, throughout a more extended range of concentration, owing to the volatility of the acid employed (*e. g.*, formic acid, acetic acid) at high temperatures.

The purity of the substances used was tested by their point of fusion. For dimethylpyrone, Poma[1] has obtained the m. p. 132°, the value obtained with the Kahlbaum specimens employed[2] was 132.1°. Most of the acids were also pure Kahlbaum samples, and gave satisfactory points of fusion without preliminary purification. Only in a few cases was it necessary to obtain a purer product by crystallization from a suitable solvent (*e. g.*, trichlorobutyric acid from ligroin) or by freezing partially an impure liquid (*e. g.*, formic acid) and rejecting the liquid portion.

The following substances were investigated:

Aliphatic acids.

1. Formic
2. Acetic
3. Chloroacetic
4. Dichloroacetic
5. Trichloroacetic
6. Trichlorobutyric
7. Trichlorolactic
8. β-Iodopropionic
9. Crotonic
10. Chlorocrotonic

Aromatic acids.

11. Benzoic
12. *o*-Toluic
13. *m*-Toluic
14. *p*-Toluic
15. α-Toluic
16. Salicylic
17. *o*-Nitrobenzoic
18. Cinnamic
19. Hydrocinnamic
20. Mandelic

Phenols, etc.

21. Phenol
22. *o*-Cresol
23. *m*-Cresol
24. *p*-Cresol
25. *o*-Nitrophenol
26. *m*-Nitrophenol
27. *p*-Nitrophenol
28. (2,4)-Dinitrophenol
29. Picric acid
30. Trinitrotoluene
31. α-Naphthol
32. β-Naphthol

Dibasic acids and phenols are not considered in the present paper. The results obtained are given in tabular and graphical form below. The freezing.point temperature is indicated by T.

1. Formic Acid.—A Kahlbaum sample froze at 7.3°. By means of repeated partial solidification, with rejection of the liquid remainder, the pure acid was obtained, melting at 8.5°.[3] With dimethylpyrone two compounds were obtained: $2C_7H_8O_2.3H.COOH$ and $C_7H_8O_2.2H.COOH$, melting at 19.6° and 19.0°, respectively; both were confirmed by analyses of the solid phases separating from the solutions. From the freezing point curve (page 1224, Fig. 1) it is evident that both compounds are considerably dissociated in the liquid state, the maxima on the curve being very flat. The following results are collected from several series of experiments:

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$...	100	85.6	76.0	65.9	60.1	54.6	50.8	47.8	45.9	44.1	43.5	43.3
T	132.1	122.5	112.5	98.0	84.5	70.9	58.1	45.0	35.1	24.9	20.4	19.0

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[1] *Gazz. chim. ital.*, 41, II, 518 (1911).

[2] For one sample the author desires to express his thanks to Professor Gomberg.

[3] Compare Ewins, *J. Chem. Soc.*, 105, 350 (1914).

(*b*) Solid phase, $2C_7H_8O_2.3H.COOH$.

% $C_7H_8O_2$	42.6	41.9	41 7	40.7	40.5	40.0	39.6	39.0	38.5	37.3	36.5	..
T	18.9	19.1	19.3	19.6	19.5	19.6	19.5	19.6	19.4	19.2	18.8	..

(*c*) Solid phase, $C_7H_8O_2.2H.COOH$.

% $C_7H_8O_2$	36.1	34.9	34 6	33 3	33.0	31.5	30.9	29.5	28.2	26.0	25.0	..
T	18.7	18.9	18.9	19 0	19.0	18.9	18.7	18.3	17 6	16.3	15.5	..
% $C_7H_8O_2$	23.9	21.5	18.9	15 3	13.6	..	.	..	..	..	..	..
T	14.3	11.1	7.0	—0 3	—4.3	.		..	..	..	..	..

(*d*) Solid phase, H.COOH.

% $C_7H_8O_2$	12.0	8 3	5 7	0		..	.	..	..	..	..	
T	—5 5	0.0	3 1	8 5				..	..	..	.	..

2. *Acetic Acid.*—From Kahlbaum's glacial acetic acid a pure product, freezing at 16.4°, was obtained by the method of partial solidification described above. With dimethylpyrone the compound $C_7H_8O_2.CH_3.$-COOH was obtained; m. p., 30° (by extrapolation). The compound is not stable at its maximum. This explains the failure of Collie and Tickle to isolate dimethylpyrone acetate, since the salt can be crystallized only from solutions containing excess of acetic acid. The composition was determined by analysis of the solid phase. The freezing point diagram is given on page 1225, Fig. 2.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	87 1	75 0	64 8	57 2	50.9	46.6	43 2	39 6	37.5
T	132 1	125.5	115 0	102 5	88.6	73 3	61 1	50.3	37 3	28.3

(*b*) Solid phase, $C_7H_8O_2.CH_3$ COOH.

% $C_7H_8O_2$	34 9	33 4	28 5	23 9	20 4	..	.	.	..	.
T	23 8	22 4	15 6	7 5	—0.4			.	.	

(*c*) Solid phase, $CH_3.COOH$

% $C_7H_8O_2$	17.7	15 3	9.0	0		..	.		.	.
T	—2 0	2 1	9 6	16.4						

3. *Chloroacetic Acid.*—This acid has been shown to exist in three[1] (perhaps four)[2] crystalline modifications, melting at 61.3°, 56.2°, 50.2° (and 43.75°), respectively. The first three of these points were experimentally confirmed with the acid employed; all other values tabulated below are on the freezing point curve of the stable modification. An equimolecular compound was obtained, melting point 39.9°, just stable at its maximum, and comparatively little dissociated.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90 5	79.9	67 2	62 8	58 4	55 2	51.8	50 8
T	132.1	126 0	116 5	97 2	87.9	75 0	63 4	46.8	41 0

(*b*) Solid phase, $C_7H_8O_2$ $CH_2Cl.COOH$.

% $C_7H_8O_2$	48 8	47 4	45 0	41 4	38 7	33 8	30.0	..	.
T	39.7	39.1	37 7	34.1	29 7	19.1	5.1		..

[1] Muller, *Z. physik. Chem.*, 86, 196 (1914).

[2] Pickering, *J. Chem. Soc*, 67, 664 (1895).

(*c*) Solid phase, $CH_2Cl.COOH$.

% $C_7H_8O_2$	27.4	23.0	17.5	9.5	0	0	0	..	..
T	14.4	27.5	41.6	53.9	61.3	56.2	50.2	..	..

4. *Dichloroacetic Acid.*—The point of fusion of this acid is still given in all books of reference as —4°, although the value +10.8° was found by Pickering.[1] The Kahlbaum sample employed gave considerable difficulty owing to persistent supercooling, but finally two freezing points were obtained:

(*a*) +9.7° (by rapid cooling with ether—carbon dioxide). Attempts at further purification of the acid did not raise this point of fusion at all.

(*b*) —4.1° (by supercooling to —10° and long stirring). Hence it appears that the acid exists in two crystalline modifications. With dimethylpyrone the compound $C_7H_8O_2.CHCl_2.COOH$ was obtained, m. p., 22.9°, just stable at its maximum. It is possible that a second compound exists but was not isolated (the curve could not be completed between 31.4–20.0% $C_7H_8O_2$, owing to the mixture supercooling to a stiff glass without crystallization).

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.9	75.5	69.0	63.6	59.8	56.4	54.1	51.5
T	132.1	124.0	111.0	99.1	85.3	72.5	56.6	43.2	26.0

(*b*) Solid phase, $C_7H_8O_2.CHCl_2.COOH$.

% $C_7H_8O_2$	50.1	47.2	43.3	40.2	35.1	31.4	..	..	..
T	22.9	21.7	17.1	11.1	—4.1	—21.2	..	..	..

(*c*) Solid phase, $CHCl_2.COOH$.

% $C_7H_8O_2$	20.0	14.1	8.1	0	0	..	..	..	..
T	—23.8	—9.0	0.8	9.7	—4.1	..	..	..	.

5. *Trichloroacetic Acid.*—The freezing point diagram is given on page 1224 (Fig. 1). Two compounds are obtained, $C_7H_8O_2.CCl_3.COOH$ (m. p. 44.8°) and $C_7H_8O_2.2CCl_3.COOH$ (m. p. 66.8°), both evidently quite stable and very little dissociated. Mixtures containing more than 60% $C_7H_8O_2$ decompose very rapidly at their melting points, with evolution of carbon dioxide, hence this part of the curve must be regarded as only approximate.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	71.4	66.1	61.1	57.6	55.5	..	..	..	..
T	132.1	124.5	110.0	99.2	83.8	67.1	52.9	..	..	..	..

(*b*) Solid phase, $C_7H_8O_2.CCl_3.COOH$.

% $C_7H_8O_2$	52.7	49.9	47.6	45.4	..	..	..	..	..	..	..
T	43.0	44.8	44.0	41.4	..	..	..	..	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2CCl_3.COOH$.

% $C_7H_8O_2$	45.4	43.2	41.0	36.9	35.5	33.8	32.0	29.5	27.1	23.6	19.7
T	36.4	46.9	54.6	63.8	65.6	66.7	66.1	63.0	58.1	49.3	33.6

(*d*) Solid phase, $CCl_3.COOH$.

% $C_7H_8O_2$	19.0	16.5	12.9	7.5	0	..	..	..	..	..	..
T	12.5	28.1	41.0	51.5	57.2	..	..	..	..	..	..

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[1] *Loc. cit.*

6. Trichlorobutyric Acid.—The curve obtained is very similar to that given by trichloroacetic acid above. Two compounds, $C_7H_8O_2.CH_3.$-$CHCl.CCl_2.COOH$ and $C_7H_8O_2.2CH_3.CHCl.CCl_2.COOH$ were obtained, melting at 56.2° and 33.8°, respectively. Mixtures containing excess of $C_7H_8O_2$ decompose slowly at their temperature of fusion, with evolution of carbon dioxide. The pure acid was obtained from a Kahlbaum sample by recrystallizations from ligroin.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.8	81.6	73.2	67.1	64.8	61.5	58.2
T	132.1	127.0	121.0	110.2	98.0	91.8	82.1	66.5

(*b*) Solid phase, $C_7H_8O_2.C_3H_4Cl_3.COOH$.

% $C_7H_8O_2$	54.4	50.4	46.1	41.2	38.8	36.8	36.6	..
T	53.4	56.1	53.8	47.8	42.5	35.2	35.1	..

(*c*) Solid phase, $C_7H_8O_2.2C_3H_4.Cl_3.COOH$.

% $C_7H_8O_2$	34.3	32.7	30.5	27.6	23.4	..	..	..
T	33.5	33.7	33.0	30.2	25.0	..	..	..

(*d*) Solid phase, $C_3H_4Cl_3.COOH$

% $C_7H_8O_2$	28.1	24.9	20.4	17.3	13.1	7.5	0	..
T	—7.2	9.7	27.1	37.1	45.9	53.0	57.9	..

7. Trichlorolactic Acid.—An equimolecular compound $C_7H_8O_2.CCl_3.$-$CHOH.COOH$ (m. p. 54.5°) was obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.0	77.7	69.2	65.0	62.2	...	..
T	132.1	126.5	113.0	92.9	77.1	65.1	..	.

(*b*) Solid phase, $C_7H_8O_2.CCl_3.CHOH.COOH$.

% $C_7H_8O_2$	58.5	55.3	50.5	44.9	41.8	39.3	36.8	33.9
T	49.5	52.7	54.4	52.6	49.8	46.9	43.6	38.5

(*c*) Solid phase, $CCl_3.CHOH.COOH$.

% $C_7H_8O_2$	33.9	30.0	26.8	22.0	17.0	10.1	0	...
T	21.2	43.2	59.3	83.0	95.4	106.6	113.8	...

8. β-Iodopropionic Acid.—Here no compound was isolated, but, from the form of the curves, it is evident that combination in the mixture has occurred. (The freezing point of each component is abnormally lowered by addition of the other; contrast with *o*-nitrophenol, page 1237.) It is possible that the melting point of the compound is so low that its curve never enters the stable region (compare *o*-toluic acid, page 1232; it is more likely, however, that supercooling persisted, preventing the isolation of the compound as the solid phase.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	75.7	65.0	57.2	50.3	44.4	..
T	132.1	123.5	108.0	87.4	67.2	44.0	18.4	..

(*b*) Solid phase, $CH_2I.CH_2.COOH$.

% $C_7H_8O_2$	41.2	37.8	31.6	27.3	23.8	20.5	11.7	0
T	8.9	18.8	35.4	45.1	52.2	58.4	70.9	81.2

9. Crotonic Acid.—An equimolecular compound, $C_7H_8O_2.CH_3.CH:CH.COOH$ is obtained; m. p. 52.2° (by extrapolation). The compound is unstable at its maximum, and crystallizes only from solutions containing excess of acid.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	87.6	76.1	62.8	54.6	49.9	45.4
T	132.1	125.5	116.5	100.7	86.0	75.2	62.3

(*b*) Solid phase, $C_7H_8O_2.C_3H_5.COOH$.

% $C_7H_8O_2$	41.0	36.8	32.8	28.7	..	..	..
T	50.0	47.5	44.1	39.2	..	..	..

(*c*) Solid phase, $C_3H_5.COOH$.

% $C_7H_8O_2$	21.3	15.8	9.0	0	..	..	..
T	49.4	56.7	63.6	71.0	..	..	..

10. α-Chlorocrotonic Acid.—The compound $C_7H_8O_2.CH_3.CH:CCl.COOH$ was obtained; m. p. 45.8°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	78.6	68.2	62.8	59.0	54.1	51.2	.	.
T	132.1	125.5	115.0	100.1	89.6	78.5	60.8	46.5	..	.

(*b*) Solid phase, $C_7H_8O_2.C_3H_4Cl.COOH$.

% $C_7H_8O_2$	49.5	46.7	43.3	40.7	38.0	37.6		.	.	
T	45.7	45.1	43.9	41.7	38.5	38.0	.	..	.	.

(*c*) Solid phase, $C_3H_4Cl.COOH$.

% $C_7H_8O_2$	38.0	35.6	35.3	34.5	31.8	28.3	25.9	19.0	10.4	0
T	39.0	46.3	47.4	49.9	57.3	65.4	71.1	82.8	92.9	99.0

11. Benzoic Acid.—The compound $C_7H_8O_2.C_6H_5.COOH$ was obtained, melting at 50.5°, and only just stable at its maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	81.1	74.2	68.5	63.5	58.9	55.9	53.0	50.5	50.0
T	132.1	127.0	120.0	111.5	102.4	93.1	82.6	74.2	63.8	53.5	50.5

(*b*) Solid phase, $C_7H_8O_2.C_6H_5.COOH$.

% $C_7H_8O_2$	50.0	49.4	47.4	45.9	43.8	...	..	...	..	..	..
T	50.5	50.5	50.2	49.6	48.5	...	...	...	..	..	..

(*c*) Solid phase, $C_6H_5.COOH$.

% $C_7H_8O_2$	41.3	37.9	34.7	30.9	25.3	18.1	9.5	0	..	..	..
T	54.8	66.8	76.7	85.6	95.2	105.2	113.6	120.8	..	..	..

12. o-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained, m. p. 48.0° (by extrapolation). The compound is unstable at its maximum; its total range of stability, from the freezing point diagram, extends only through 2% of the concentration range.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.1	80.5	70.2	64.9	60.5	55.7	51.1	48.3	45.1	44.9
T	132.1	126.0	117.5	104.0	94.9	86.1	74.6	62.0	53.4	43.6	43.0

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$	45.2	44.3	43.8	.	..	..	..	..	..	...	..
T	47.2	46,6	46.2	...	..	..	..	..	..	...	..

(*c*) Solid phase, $C_7H_7.COOH$.

% $C_7H_8O_2$	44.9	43.8	42.2	40.1	35.4	29.6	20.7	10.5	0	...	..
T	43.0	46.2	50.4	55.7	66.0	77.2	89.3	97.8	103.4	...	..

13. m-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained, melting at 64.1°. In common with the other compounds derived from the similar acids in 11, 12 and 14, this compound is considerably dissociated in the liquid state, as is shown by the flatness of the maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.0	79.0	68.6	64.4	58.6	54.0
T	132.1	126.5	116.0	102.0	94.4	81.0	69.1

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$	51.9	49.1	45.3	42.5	40.1	..	..
T	63.8	64.0	62.9	61.7	60.5	...	..

(*c*) Solid phase, $C_7H_7.COOH$.

% $C_7H_8O_2$	37.5	33.2	26.3	18.6	9.9	0	..
T	59.8	70.0	84.8	95.6	103.0	107.6	..

14. p-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ (m. p. 88.0°, by extrapolation) was obtained. This compound is unstable at its maximum, and crystallizes only from solutions containing excess of dimethylpyrone. In this respect it is unique among the unstable compounds here obtained, since all others are crystallized from solutions with excess of acid. The difference is due merely to the very high point of fusion of the *p*-toluic acid. The freezing point curve of the system is given on page 1225, Fig. 2.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	87.3	79.2	72.6	67.4	63.0	60.1
T	132.1	126.5	120.0	112.0	103.1	93.4	86.3

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$

% $C_7H_8O_2$	59.5	57.2	55.0	53.2	.	..	...
T	85.0	86.2	87.1	87.7	..	..	...

(*c*) Solid phase, $C_7H_7.COOH$.

% $C_7H_8O_2$	50.6	47.3	41.4	32.1	21.4	10.3	0
T	93.2	106.9	124.4	143.2	158.6	170.0	178.5

15. Phenylacetic Acid (α-toluic acid).—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained; m. p. 24.6° (by extrapolation). The compound is unstable at its maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.0	76.3	70.1	64.4	60.0	54.1	48.9	47.0	43.4	40.2
T	132.1	125.0	113.0	105.5	94.9	85.1	69.0	51.6	44.2	25.4	5.5

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$	41.1	40.2	38.5	38.0	..	..	..	..	..	..	..
T	21.7	21.0	19.2	18.7	..	..	..	..	..	..	..

(*c*) Solid phase, $C_7H_7.COOH$.

% $C_7H_8O_2$	36.0	34.3	30.1	23.6	16.4	8.0	0	..	..	..	..
T	19.2	25.9	37.8	51.6	62.4	70.8	76.7	..	..	..	..

16. *Salicylic Acid.*—The compound $C_7H_8O_2.C_6H_4.OH.COOH$ was obtained, m. p. 71.9°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.1	79.3	67.8	63.4	60.4	57.3
T	132.1	128.0	119.5	100.5	89.2	80.1	68.9

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.OH.COOH$.

% $C_7H_8O_2$	56.0	53.5	51.1	49.9	47.5	44.0	...
T	69.1	70.7	71.6	71.9	71.1	68.9	...

(*c*) Solid phase, $C_6H_4.OH.COOH$.

% $C_7H_8O_2$	43.2	39.3	32.7	27.7	17.4	10.1	0
T	70.3	92.1	115.8	127.6	144.2	152.2	158.9

17. *o-Nitrobenzoic Acid.*—The compound $C_7H_8O_2.C_6H_4.NO_2.COOH$, melting at 72.3°, was obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	86.5	75.4	68.6	64.3	60.1
T	132.1	123.0	111.0	98.9	90.1	76.3

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.COOH$

% $C_7H_8O_2$	57.0	52.1	49.9	46.9	43.9	40.8
T	68.9	71.6	72.3	71.6	69.6	66.1

(*c*) Solid phase, $C_6H_4.NO_2.COOH$

% $C_7H_8O_2$	37.7	34.2	28.6	21.0	11.5	0
T	76.1	90.5	108.4	124.9	137.4	147.0

18. *Cinnamic Acid.*—The compound $C_7H_8O_2.C_6H_5.CH : CH.COOH$ (m. p. 73.2°) was obtained. The system is represented graphically on page 1224, Fig. 1. It is evident that the compound formed is considerably dissociated in the liquid state.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.2	81.0	71.9	64.3	60.6	56.9	54.3
T	132.1	126.5	119.5	107.8	95.7	88.4	79.9	72.7

(*b*) Solid phase, $C_7H_8O_2.C_8H_7.COOH$.

% $C_7H_8O_2$	52.0	50.0	48.2	44.6	...	...	...	...
T	73.1	73.2	73.1	72.4	...	...	...	...

(*c*) Solid phase, $C_8H_7.COOH$.

% $C_7H_8O_2$	43.5	40.3	36.3	30.5	24.8	15.9	9.1	0
T	75.0	87.0	97.4	109.0	116.4	126.3	131.8	136.8

19. *Hydrocinnamic Acid.*—Here no compound was isolated. The freezing point diagram of the system, however, indicates the presence of a compound in the solution (compare β-iodopropionic acid, page 1231).

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.9	80.2	72.3	69.4	66.0	63.0	59.5	56.7	53.1	50.2
T	132.1	126.5	119.0	110.0	105.4	99.5	93.3	86.7	80.1	69.7	60.6
% $C_7H_8O_2$	47.0	43.3	39.9	36.6	...	..	.	.	..	..	
T	49.7	35.3	22.0	4.8	...	..	..	..	..	..	..

(*b*) Solid phase, $C_8H_9.COOH$.

% $C_7H_8O_2$	33.7	26.7	21.1	15.3	8.6	5.0	0	.	..	..	..
T	5.9	21.1	29.4	35.8	41.0	43.2	45.2	.		..	..

20. Mandelic Acid.—Two compounds were obtained: $C_7H_8O_2.C_6H_5.$-$CHOH.COOH$ (m. p. 69.3°) and $C_7H_8O_2.2C_6H_5.CHOH.COOH$ (m. p. 74.0°). The solutions of this system exhibit supercooling to a marked degree, consequently it was found possible to follow all the curves into their unstable regions, and to obtain several freezing points for the same mixture, according to the solid phase separating out. Results are shown in diagram form on page 1224, Fig. 1.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.5	81.0	76.0	72.4	67.5	62.4	58.4	55.9	..	.	.
T	132.1	123.5	116.0	109.7	104.7	94.8	82.0	68.1	66.4	..	.	.

(*b*) Solid phase, $C_7H_8O_2.C_6H_5.CHOH.COOH$.

% $C_7H_8O_2$	56.1	54.6	52.1	50.0	47.3	44.5	42.8	39.3	36.6	.	.	.
T	66.5	67.5	68.9	69.3	68.8	67.2	66.1	62.9	60.0		.	.

(*c*) Solid phase, $C_7H_8O_2\,2C_6H_5.CHOH\,COOH$.

% $C_7H_8O_2$	54.6	50.0	44.5	43.5	41.3	39.3	36.6	34.3	33.3	32.8	32.5	30.5
T	49.0	59.3	67.2	67.9	70.0	71.7	72.7	73.8	74.0	73.7	73.6	73.0

(*d*) Solid phase, $C_6H_5.CHOH.COOH$.

% $C_7H_8O_2$	36.6	32.5	30.5	28.4	25.3	18.8	10.6	0	.	..	..	..
T	61.7	73.6	78.2	82.8	88.6	98.5	108.0	117.0	..	.	..	..

21. Phenol.—No addition compounds of dimethylpyrone with phenols have been previously described. On examination, however, it was found that such compounds existed, and were little dissociated in the liquid state, the maxima obtained being usually quite sharp. With phenol itself the compound $C_7H_8O_2.2C_6H_5.OH$ was obtained, with m. p. 36.8°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.1	77.5	68.4	60.8	53.7	50.9	48.4	45.4
T	132.1	126.0	116.0	103.5	88.9	69.1	59.3	46.6	32.1

(*b*) Solid phase, $C_7H_8O_2.2C_6H_5OH$.

% $C_7H_8O_2$	43.1	40.4	38.5	35.4	32.6	29.3	24.8	21.2	18.5
T	28.0	32.0	34.1	36.1	36.7	35.6	29.7	22.3	15.6

(*c*) Solid phase, C_6H_5OH.

% $C_7H_8O_2$	13.8	8.4	0	..	..	..	..	..	..
T	16.6	31.3	42.4	. .		..	..	..	.

22. o-Cresol.—Here two addition compounds were obtained: $C_7H_8O_2.$-$C_7H_7.OH$, melting at 54.4°, and $C_7H_8O_2.2C_7H_7.OH$, melting at 50.4°, both compounds are stable at their maxima. (See diagram, page 1240, Fig. 3.)

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	80.0	69.5	61.4	55.2	52.4	..	..
T	132.1	126.5	119.5	105.5	91.1	74.3	64.0	..	..

(*b*) Solid phase, $C_7H_8O_2.C_7H_7OH$.

% $C_7H_8O_2$	49.2	46.6	43.1	39.6	..	..	..	..	..
T	54.3	53.5	51.5	47.2	..	..	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	39.6	36.6	33.4	29.5	24.0	20.6	17.2	15.2	13.9
T	47.2	49.4	50.4	49.2	43.2	37.8	27.5	21.8	16.6

(*d*) Solid phase, $C_7H_7.OH$.

% $C_7H_8O_2$	13.9	11.0	5.5	0	..	..	..	..	..
T	16.6	21.0	26.9	30.3	..	..	..	..	..

23. m-Cresol.—The compound $C_7H_8O_2.2C_7H_7.OH$ was obtained; m. p. 25.4°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	74.4	64.8	58.7	53.6	50.0	45.9	43.9	41.0
T	132.1	123.0	112.0	97.2	84.2	69.8	55.6	35.3	24.7	4.3

(*b*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	41.6	38.2	34.7	32.0	28.4	23.0	19.0	14.3	..	..
T	21.3	23.9	25.0	25.3	23.7	17.4	9.5	—5.0	..	..

(*c*) Solid phase, C_7H_7OH.

% $C_7H_8O_2$	9.5	4.8	0	..	..	..	..	...	..	..
T	—1.2	6 1	10.9	..	..	..	..	..	..	..

24. p-Cresol.—Two compounds were obtained: $C_7H_8O_2.C_7H_7.OH$ (m. p. 29.5°, by extrapolation) and $C_7H_8O_2.2C_7H_7OH$ (m. p. 20.3°). The former compound is unstable at its maximum point. The form of the curve indicates strongly the presence of a third compound of the formula $C_7H_8O_2.4C_7H_7.OH$, but it was not found possible to isolate a compound of the composition, since the mixture of this composition supercools to a hard, glassy mass, and no freezing point can be obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88 5	77.2	67.6	61.4	54.9	51.0	48.2	44.9
T	132.1	125.5	115.0	102.0	90.2	73.6	59.6	46.6	31.8

(*b*) Solid phase, $C_7H_8O_2.C_7H_7OH$.

% $C_7H_8O_2$	41.5	38.7	37.0	...	..	..	..	..	..
T	25.7	22.4	19.6	...	..	..	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	35.8	33.2	31.6	29.2	25.9	23.3	..	..	..
T	19 6	20.3	19.7	17.5	11.2	1.2	..	..	..

(*d*) Solid phase, C_7H_7OH.

% $C_7H_8O_2$	17.1	13.3	7.1	0	..	..	..	..	..
T	—0.5	14.6	26.6	34.1	..	..	..	..	..

25. o-Nitrophenol.—With this system the peculiar result was obtained that, not only could no compound be isolated, but the form of the curve shows conclusively that none exists in solution. The results are shown in graphic form, together with those of the other mononitrophenols, which exhibit quite different behavior, on page 1240, Fig. 3. It is evident that *o*-nitrophenol and dimethylpyrone have no tendency to form addition products; this is perhaps due to the influence of the nitro group in the *o*-position.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.4	79.7	68.0	61.5	56.1	51.3	46.8	42.2	37.3	32.3	27.5
T	132.1	126.5	119.0	110.4	104.9	98.6	92.9	85.9	77.9	68.3	57.1	45.8

(*b*) Solid phase, $C_6H_4.NO_2.OH$

% $C_7H_8O_2$	22.7	18.7	13.2	7.6	0	..	..	.	.	..	..	..
T	32.7	35.1	38.2	41.0	44.7	..	..	..	.	..	..	..

26. m-Nitrophenol.—The compound $C_7H_8O_2.C_6H_4.NO_2.OH$, melting at 68.8°, was obtained.

(*a*) Solid phase, $C_7H_8O_2$

% $C_7H_8O_2$	100	90.6	80.7	70.3	65.3	61.0	57.4	..	..
T	132.1	127.0	118.5	104.2	93.8	81.5	67.0	..	..

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	53.8	50.8	48.3	45.4	42.1	39.2	36.2	33.0	31.5
T	68.1	68.7	68.4	66.9	63.0	58.8	52.9	45.9	42.6

(*c*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	29.0	25.1	20.4	14.5	8.4	0		.	.
T	52.4	63.4	72.9	82.9	89.7	95.3		.	.

27. p-Nitrophenol.—Two compounds were obtained: $C_7H_8O_2.C_6H_4.NO_2.OH$, melting at 72.3°, and $C_7H_8O_2.2C_6H_4.NO_2.OH$, melting at 58.2°. Both compounds are stable at their maxima.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.1	77.0	68.8	64.6	60.8	57.8
T	132.1	125.5	114.5	101.3	91.4	80.2	68.3

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.OH$

% $C_7H_8O_2$	57.2	53.5	50.6	47.2	43.8	40.4	37.4
T	68.3	71.3	72.2	70.9	67.2	62.1	56.4

(*c*) Solid phase, $C_7H_8O_2.2C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	37.4	34.3	33.6	32.9	31.6	30.0	..
T	57.0	58.1	58.2	58.1	57.9	57.4	...

(*d*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	30.0	28.2	26.2	22.4	15.5	9.1	...
T	57.4	65.4	72.2	82.2	96.6	105.2	113.8

28. 2,4-Dinitrophenol.—The compound $C_7H_8O_2.C_6H_3.(NO_2)_2.OH$ was obtained; m. p. 78.4°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.4	80.1	69.9	63.9	58.2	...
T	132.1	126.0	118.0	105.6	95.2	83.2	...

(*b*) Solid phase, $C_7H_8O_2.C_6H_3.(NO_2)_2.OH$.

% $C_7H_8O_2$	55.2	51.8	48.1	45.0	41.8	...	...
T	77.5	78.3	78.1	77.5	75.8	...	...

(*c*) Solid phase, $C_6H_3.(NO_2)_2.OH$.

% $C_7H_8O_2$	37.7	34.8	31.9	25.1	17.1	9.3	0
T	75.0	81.1	86.3	95.1	102.9	109.0	114.0

29. Picric Acid.—The compound $C_7H_8O_2.C_6H_2(NO_2)_3.OH$ was obtained; point of fusion, 100.8°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.0	78.7	74.4	70.6	67.5	...	...	...	..	..	..
T	132.1	124.0	111.2	101.1	90.0	83.5	...	...	...	..	..	..

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.(NO_2)_3.OH$.

% $C_7H_8O_2$	66.7	65.2	63.8	61.9	59.5	55.7	52.6	50.0	47.7	43.6	38.4	34.1
T	81.9	86.7	89.5	92.9	96.1	98.9	100.2	100.8	100 4	98.8	94.9	87.6

(*c*) Solid phase, $C_6H_2.(NO_2)_3.OH$.

% $C_7H_8O_2$	30.0	26.1	22.4	15.5	9.6	0	...	...	...	..	..	..
T	87.5	92 4	97 4	104 8	110.6	118.4	...	...	...	..	..	..

30. Trinitrotoluene.—The pseudo-acid trinitrotoluene was examined with dimethylpyrone, but no indication of compound formation could be observed. The curve resembles that of *o*-nitrophenol.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	86.3	75.3	65.0	57.2	51 1	46.1	41 0	35.4
T	132.1	124.5	115.5	105.3	97.5	90.3	84.0	77.6	70.2

(*b*) Solid phase, $C_7H_5.(NO_2)_3$.

% $C_7H_8O_2$	29.1	24.1	15.6	7.8	0	..	..	..	..
T	64.2	67.4	72.4	76.7	80.7	..	..	..	..

31. α-Naphthol.—Interesting results were obtained with the naphthols; the freezing point diagrams are given on page 1225, Fig. 2. α-Naphthol gives two compounds with dimethylpyrone: $C_7H_8O_2.C_{10}H_7.OH$ (m. p. 69.8°, by extrapolation), and $2C_7H_8O_2.3C_{10}H_7.OH$ (m. p. 79.1°). The former is unstable at its maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.0	77.7	68.8	60.5	56.9	..	..
T	132.1	126.0	116.5	103.6	85.2	73.0	..	..

(*b*) Solid phase, $C_7H_8O_2.C_{10}H_7OH$.

% $C_7H_8O_2$	54.1	53.0	51.5	...	..	..	..	..
T	65.6	67.8	69.3	...	..	..	..	..

(*c*) Solid phase, $2C_7H_8O_2.3C_{10}H_7.OH$.

% $C_7H_8O_2$	50.0	48.8	47.3	45.3	42.7	40.6	38.8	37.3
T	70.5	73.2	75.6	77.4	78.3	79.0	78.8	78.4
% $C_7H_8O_2$	35.8	34.4	32.0	29.8	27.9	25.0	..	..
T	77.6	76.8	73.8	69.7	65.9	56.6	..	..

(*d*) Solid phase, $C_{10}H_7.OH$.

% $C_7H_8O_2$	23.4	20.7	17.7	12.0	6.2	0	..	..
T	56 0	65.7	73.8	84.2	90.7	96.1	..	..

32. *β-Naphthol.*—Two compounds were obtained: $2C_7H_8O_2.3C_{10}H_7.OH$ (m. p. 39.5°) and $C_7H_8O_2.2C_{10}H_7OH$ (m. p. 44.6°). The former compound is unstable at its maximum point, but, owing to the readiness with which solutions of this system exhibited persistent supercooling, it was found possible to carry the curve some distance into its unstable region. (See diagram, page 1225, Fig. 2.)

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	87.6	76.3	66.6	61.6	57.2	55.4	52.1	49.3	46.5
T	132.1	126.0	114.5	99.5	87.1	74.5	68.2	54.9	40.7	24.3

(*b*) Solid phase, $2C_7H_8O_2.3C_{10}H_7OH$.

% $C_7H_8O_2$	46.5	44.7	43.8	42.2	40.6	37.3	35.0	..	..	..
T	36.6	38.0	38.4	39.0	39.4	38.8	37.4	..	..	..

(*c*) Solid phase, $C_7H_8O_2\ 2C_{10}H_7OH$.

% $C_7H_8O_2$	43.8	40.2	38.1	35.9	33.6	33.0	...	..	..	..
T	34.4	40.3	42.5	43.9	44.5	44.6	...	..	..	..

(*d*) Solid phase, $C_{10}H_7OH$.

% $C_7H_8O_2$	30.2	27.3	25.1	21.4	14.1	9.6	0	..	..	..
T	54.5	70.6	79.9	92.0	107.9	113.8	121.6	..	..	..

Consideration of Results.

Thirty-two organic substances of acidic nature have been examined with dimethylpyrone, and the existence of thirty-seven addition compounds has been indicated by the freezing point curve. These compounds may be divided into three classes:

(*a*) 24 of the general type $C_7H_8O_2.HX$.
(*b*) 3 of the general type $2C_7H_8O_2.3HX$.
(*c*) 10 of the general type $C_7H_8O_2.2HX$.

No instances of the formation of compounds containing excess of dimethylpyrone, or of mixed crystals, were observed.

The addition compounds exhibited, in general, beautiful crystalline structure, either in the form of needles radiating from a common center, star-clusters, or lustrous plates. Consequently, in practically all of the systems examined, it was extremely easy to identify changes in the solid phase.

The melting points of the compounds are usually much below those of their components. The few exceptions are to be found in those cases where the melting point of one component is also very low.

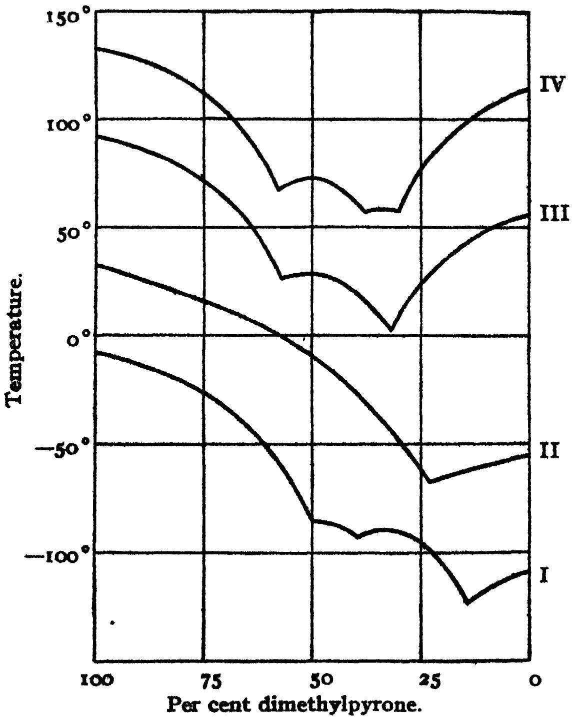
It is interesting to compare the difference in behavior of isomeric substances examined. As examples the following may be noted:

I. o-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ crystallizes only from solutions containing excess of acid. *m-Toluic acid.* The compound formed is stable at its maximum. *p-Toluic acid.* The compound crystallizes only from solutions containing an excess of dimethylpyrone.

II. o-Nitrophenol.—No compound is formed. *m-Nitrophenol.* The compound $C_7H_8O_2.C_6H_4.NO_2OH$ is formed. *p-Nitrophenol.* Two compounds: $C_7H_8O_2.C_6H_4NO_2.OH$ and $C_7H_8O_2.2C_6H_4NO_2.OH$ are formed.

III. α-Naphthol.—The compounds $C_7H_8O_2.C_{10}H_7OH$ and $2C_7H_8O_2.3C_{10}H_7OH$ are formed. *β-Naphthol.* The compounds $2C_7H_8O_2.3C_{10}H_7OH$ and $C_7H_8O_2.2C_{10}H_7OH$ are obtained.

Particular attention is due to those compounds isolated, which are unstable at their maximum. These cannot be obtained at all by the simple method of mixing the components in the required proportions. The freezing point curve gives, however, all the necessary data for the preparation of such a compound. For example, dimethylpyrone acetate, which Collie and Tickle failed to isolate, may readily be obtained as follows (see diagram, page 1225, Fig. 2). A mixture of 35% dimethylpyrone and 65% acetic acid (molecular percentages) is taken. This melts at 24°, and, on cooling, the solid phase separating out is the equimolecular compound. The best yield may be obtained by cooling to 0°, filtering off the remaining liquid, and drying the crystals with filter paper. The compound thus obtained melts at 30°, at the same time decomposing into its components and depositing dimethylpyrone.



I. *o*-Cresol. Add 140° to temperature scale.
II. *o*-Nitrophenol. Add 100° to temperature scale.
III. *m*-Nitrophenol. Add 40° to temperature scale.
IV. *p*-Nitrophenol. Temperature scale correct.

Fig. 3.

The addition compounds obtained are always more or less dissociated into their components in the liquid state. For the acids examined, the rule holds, in general, that the extent of dissociation is greater, the weaker the acid is. The degree of dissociation may be approximately determined by the sharpness of the maximum, *i. e.*, the decrease in the temperature of fusion of the compound on addition of either component. If dissociation is slight the decrease is rapid, with more highly dissociated compounds the decrease is small and may even (in extreme cases) be converted into an increase.[1]

The following table shows the decrease in the temperature of fusion of the equimolecular compounds of dimethylpyrone and acid, due to the addition of 5% of acid, for all cases where data are available from the results given above. The dissociation constants of the acids[2] are included for comparison.

Acid.	T(50% $C_7H_8O_2$)—T(45% $C_6H_8O_2$).	100 K.
Chloroacetic	2.2°	0.155
Dichloroacetic	3.2	5.14
Trichloroacetic	4.3	121.0
Trichlorobutyric	3.5	10.0
Trichlorolactic	1.8	0.465
α-Chlorocrotonic	1.3	0.072
Benzoic	1.2	0.0060
m-Toluic	1.2	0.00514
Salicylic	2.1	0.102
o-Nitrobenzoic	1.8	0.616
Cinnamic	0.6	0.00355
Mandelic	1.6	0.0417

The connection between the degree of dissociation of the compound and the strength of the acid is made quite evident from the above figures; the two extreme cases (trichloroacetic and cinnamic acids) are illustrated in the diagram on page 1224, Fig. 1. The relation is important, but can, however, only be approximate, since for the acidic strengths we should compare values, not in aqueous solution, but in dimethylpyrone.[3] The dissociation of the compounds is also compared at their various points of fusion, whereas the temperature factor is important in regard to the degree of dissociation of addition compounds.[4]

The tendency to form addition products is greatest at low temperatures; this is well illustrated in the case of hydrates. The effect of temperature is best seen, in the results of the present investigation, in the compounds formed from phenol and its derivatives. These are little dissociated into their components in spite of the weak acidic nature of the substances employed, owing, in general, to their low temperatures of fusion. Temperature seems, indeed, to be more important here than acidic strength, thus (to compare the stable 50% compounds) the compound of *o*-cresol is less dissociated than that of dinitrophenol, or even than that of picric acid, both of which have considerably higher melting points.

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[1] Kremann, *Monats.*, 25, 1222 (1904).

[2] Ostwald, *Z. physik. Chem.*, 3, 418 (1889).

[3] The researches of Walden indicate that the general order of acidic strengths in two solvents will be the same, although exceptions are to be found. That dimethylpyrone is a good ionizing medium has been shown by Poma, *Gazz. chim. ital.*, 41, II, 518 (1911).

[4] The heat of fusion of the compound, which will vary in different cases, is also to be considered.

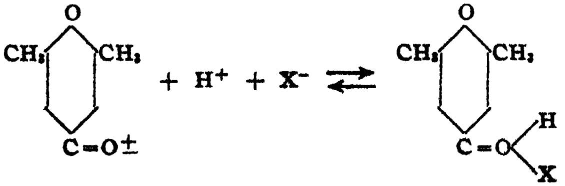
Constitution of Dimethylpyrone and its Addition Compounds.—It remains to discuss the bearing of the results obtained on the several hypotheses as to the constitution of dimethylpyrone and its addition products, considered in the introduction.

The difficulty of representing the structural formulae of compounds, more complex than equimolecular, except under the scheme (I), has already been mentioned. The thirteen compounds of the general types $2C_7H_8O_2.3HX$ and $C_7H_8O_2.2HX$, obtained in the research, cannot be accounted for by (II) or (III), but may readily be expressed structurally according to (I).

The mixture acid-dimethylpyrone was, in every system studied, colored. The color varied from pale yellow (with weak acids) to dark red (with strong acids). In this connection the view of Vorländer and Mumme,[1] that the change of color is due to a change in the degree of saturation of one or more elements composing the substances, is of importance.

A further point to be noticed is that the reaction between dimethylpyrone and acids is instantaneous. In no case could it be observed that the freezing point of a mixture changed at all with time; equimolecular mixtures gave the same point of fusion immediately after preparation as after several days. Similarly Baeyer and Villiger,[2] who first stated that time was necessary for the formation of dimethylpyrone hydrochloride, subsequently[3] withdrew this statement. Now, an organic reaction of the type (II), involving the breaking up of the simple acid molecule as well as of the carbonyl oxygen linkage, would probably be a time reaction. On the other hand, ionic reactions are *essentially* instantaneous.

We may consider the formation of the addition product $C_7H_8O_2.HX$ as proceeding as follows:



(IV)

Dimethylpyrone is here regarded as the ionizing medium,[4] and the carbonyl oxygen as primarily active. Formation of the more complex compounds involves the activity of the second oxygen atom.

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[1] *Ber.*, 36, 1470 (1903).

[2] *Ibid.*, 34, 2679 (1901).

[3] *Ibid.*, 35, 3612 (1902).

[4] The fact that dimethylpyrone is a good ionizing medium is also an indication of its unsaturated character. See Stieglitz, "Qualitative Chemical Analysis," Part I, 1912, p. 64, and Kendall, THIS JOURNAL, 36, 1069 (1914).

This view is supported by the fact that the equilibrium point of the above reversible reaction (*i. e.*, the extent of dissociation of the addition compound formed into its components) is a function of the acidic strength, as has been demonstrated above. The stronger the acid is, the more completely does the reaction from left to right proceed. In agreement with this, also, is the extent of color change on mixing the components; for example, cinnamic acid with dimethylpyrone gives the faintest tinge of yellow, while trichloroacetic acid gives a dark red solution.

The results of this investigation point, therefore, in favor of the assumption that the addition compounds of dimethylpyrone with acids are true oxonium salts, in which oxygen functions as a quadrivalent atom. The equilibrium of the reaction is best represented as in (IV) above.

In conclusion, the advantages of the method followed above, for the general study of addition reactions, may be pointed out. Its first advantage is its rapidity; after the technique has been mastered, a system presenting no special difficulties can easily be completed in two days. Secondly, it indicates *all* compounds formed between the components chosen, including such compounds as are not stable at their maxima and cannot be obtained by the ordinary methods. In few cases is a special analysis of the solid phase necessary, the composition of the compounds obtained is read directly from the freezing point curve.[1] It is possible that sometimes a compound cannot be isolated owing to supercooling; however, its existence may be recognized by the form of the curves. Finally the curves indicate also the degree of dissociation of the compounds into their simple components.

The method is being extended to other similar systems. It is hoped, also, that further evidence as to the nature of these reactions will be obtained from conductivity measurements.

Summary.

The freezing point curves of monobasic organic acids and phenols with dimethylpyrone have been examined. The existence of a large number of addition compounds has been demonstrated.

A consideration of the results obtained leads to the view that the reaction is ionic, and that the compounds formed are true oxonium salts.

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[1] Cases of "solid solutions" may be recognized by the fact that any maximum on the freezing point curve will not be (except by chance) at a point of simple molecular composition

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA.]

THE NITROSULFONIC ACIDS OF *p*-XYLENE.

BY WILLIAM J. KARSLAKE AND RALPH C. HUSTON.

Received April 3, 1914

1. Introduction.

Nolting and Kohn[1] record the preparation of an aminosulfonic acid of *p*-xylene to which they ascribe the formula:

$$C_6H_2\overset{1,4}{(CH_3)_2}\overset{6}{NH_2}\overset{2}{SO_3H}$$

This acid was prepared by reducing with ammonium sulfide, or with tin and hydrochloric acid, the solution resulting from the treatment of *p*-xylenesulfonic acid with red, fuming nitric acid. The nitro-acid was not isolated, nor were any of its derivatives prepared.

Guy G. Frary[2] describes a nitrosulfonic acid of *p*-xylene which he prepared by nitrating *p*-xylenesulfonic acid with nitric acid (sp. gr. 1.60) in the cold. The potassium, sodium, calcium, barium, strontium, magnesium, copper, and zinc salts were prepared and of these the potassium, barium, copper, and zinc salts were analyzed. Most of these were prepared from the crude acid solution and were purified with difficulty. Frary assigned the formula $C_6H_4\overset{1,4}{(CH_3)_2}\overset{6}{NO_2}\overset{2}{SO_3H}$ to the acid, in spite of the fact that an attempt to reduce it to the amino acid with ammonium sulfide proved unsuccessful. Attempts to prepare the sulfonchloride from the free acid, or from its potassium salt, resulted in the formation of a reddish brown oil which failed to solidify under water, and which did not crystallize from organic solvents. Somewhat better success attended the attempts to prepare the sulfonchloride of the nitrosulfonic acid by nitrating the sulfonchloride of *p*-xylene with nitrosulfuric acid. Two nitrosulfonchlorides were obtained, one in quantities large enough for analysis, the other, and more soluble one, in an insufficient quantity. The first melted at 109.5° and gave an amide melting at 179°. The second melted at 56–57° and gave an amide melting at 199–200°.

With the hope of obtaining a more thorough knowledge of the nitrosulfonic acids of *p*-xylene, the following research was undertaken. The problem was attacked in two ways, the initial material in each case being "Kahlbaum's" *p*-xylene. In one series of experiments *p*-xylene was sulfonated, and various methods of nitration were tried on the sulfonic acid or on its chloride. In the other series, a nitro group was introduced into *p*-xylene and the nitro-*p*-xylene treated with different concentrations of sulfuric acid or with chlorosulfonic acid.

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[1] *Ber.*, 19, 141 (1886).

[2] An unpublished Master's Thesis, State University of Iowa, 1909.

2. Experimental.

Sulfonation of p-Xylene.—*p*-Xylene may be sulfonated by means of strongly fuming sulfuric acid.[1] 500 g. of *p*-xylene, in a glass stoppered bottle, were treated with 650 g. of fuming sulfuric acid (25% anhyd.). The acid was added in small portions at a time, the mixture being constantly shaken. Considerable heat was evolved. On standing over night about three-fourths of the *p*-xylene dissolved. 75 g. more of the acid were added and the mixture turned three hours in a rotater, at the end of which time sulfonation was complete. The light brown syrupy mass was poured into an equal volume of water (1075 cc.) and allowed to stand over night. The separated acid was filtered off by suction and dried on porous plates. Yield, 770 g. The mother liquor yielded, on being heated two hours and cooled, a second crop of crystals which weighed 220 g., making a total of 990 g. of the crude sulfonic acid. A third crop of crystals, which tended to come down in radiating tufts, was obtained from the mother liquor. This latter compound was not studied further.

Nitration of p-Xylenesulfonic Acid.—The crude crystals of *p*-xylenesulfonic acid, which contained some sulfuric acid, were nitrated in the cold with fuming nitric acid, or with nitrosulfuric acid. In some cases the nitrating agent was added to the crude solution of sulfonic acid, no previous precipitation being made. The best yield was obtained by the following method: 100 cc. of the syrupy solution produced by the sulfonation of *p*-xylene were treated with nitric acid (sp. gr. 1.51), drop by drop, until 45 cc. had been added. The containing flask was cooled in ice. The reaction proceeded smoothly with evolution of red fumes. The solution was allowed to stand over night. After being evaporated on the water bath until red fumes ceased to be evolved, it was poured into 600 cc. of water. A small amount of dinitro-*p*-xylene was filtered off and the solution again evaporated to 110 cc. An equal volume of saturated potassium chloride solution was added and the mixture allowed to stand two days. The potassium salts were then filtered off and air dried. Yield, 64 g.

Action of Phosphorous Pentachloride on the Potassium Salts of the Nitrosulfonic Acids.—Frary's failure to obtain crystalline sulfonchlorides by the action of phosphorous pentachloride on the crude potassium salts of the nitrosulfonic acids is hard to understand. In this investigation eleven experiments, in which the dry potassium salts were treated with phosphorous pentachloride under different conditions, were made. All of the experiments yielded two sulfonchlorides, one melting at 109.5° and a more soluble one melting at 60°, while four of the eleven yielded, in addition, a third sulfonchloride, in very small amounts, which melted at 75°. The best yields were obtained under the following conditions: 150 g. of the crude, powdered potassium salts of the nitrated sulfonic acid, dried at 110°, were treated with 200 g. of phosphorous pentachloride. Heat was evolved and the whole mass slowly liquefied. After standing two hours the containing flask was heated one hour on a water bath. The heavy oily liquid was poured into ice water, washed thoroughly, and allowed to stand under ice water two days. It did not solidify but became granular in appearance and of the consistency of a thick paste. After the water was drained off the paste was dissolved in 1000 cc. of ether and dried over calcium chloride. Most of the ether was distilled off and the residue transferred to a beaker. Crystals began to form almost immediately although very slowly. After standing ten days the crystals were filtered off by the aid of a suction pump and washed with a mixture of ether and petroleum ether. Yield, 10 g. From this batch of crystals, upon recrystallization from ether and petroleum ether, there were obtained two sulfonchlorides; 9.6 g. of one which gave a melting point of 109.5° and 0.2 g. of a slightly more soluble one which melted at 74.5°. (In one case the separation of the two sulfonchlorides was made mechanically.) The mother liquor from the first crop of crystals was placed in an ice box for three weeks, when a second crop of crystals was filtered off. This crop gave, on recrystallization, 2.3 g. of the sulfonchloride melting at 109.5° and 3.1 g. of a decidedly more soluble sulfonchloride of the same crystalline form which, after repeated recrystallization, melted at 60°. A third crop of crystals of the sulfonchloride melting at 60° was obtained. Yield, 10.4 g. The remaining 14 g. of reddish oil did not yield crystals on standing three months. When treated with ammonium hydroxide it gave an amide which melted, after seven crystallizations from alcohol and water, at 147°, a close agreement with the melting point of *p*-xylene-sulfonamide.

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[1] Fittig and Glinzer, *Ann.*, 136, 305 (1865); Jacobson, *Ber.*, 10, 1009 (1877).

Total yield of the nitrosulfonchloride melting at 109 5° = 11 9 g.
Total yield of the nitrosulfonchloride melting at 75.0° = 0.2 g.
Total yield of the nitrosulfonchloride melting at 60.0° = 13.5 g.

An attempt to increase the rate of precipitation of the low melting nitrosulfonchloride by dissolving the oil in ether, shaking with dilute ammonium hydroxide, neutralizing with hydrochloric acid, drying and evaporating, was not successful.

Recrystallization of the crude potassium salts from alcohol did not increase the yield of nitrosulfonchlorides to an appreciable extent.

Attempts to nitrate the sulfonchloride of *p*-xylene by means of nitric acid, nitrosulfuric acid, or diacetyl-orthonitric acid[1] met with only limited success. In all trials but one, only one sulfonchloride, and that in small quantities, was produced, *i. e.*, the one melting at 109.5°. In one case a very small yield of the sulfonchloride melting at 60° was isolated. A rather large excess of nitrosulfuric acid gave the best results.

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[1] *Ber.*, 35, 2526 (1902).

Sulfonation of Nitro-p-xylene.—*p*-Xylene was nitrated[1] in the cold with fuming nitric acid (sp. gr. 1.60). The nitro-*p*-xylene was purified by steam distillation.

Attempts to sulfonate this compound with concentrated or fuming sulfuric acid at room temperature, or at the temperature of boiling water were unsuccessful. Either no appreciable reaction took place, or a violent reaction set in which changed the reacting mixture to a charred mass.

Chlorosulfonic acid has been found to be an effective reagent in producing the sulfonic acids[2] and the sulfonchlorides[3] of aromatic nitro derivatives. Speaking generally, the nitro derivatives of the aromatic hydrocarbons, when heated with two or more mols of chlorosulfonic acid, produce sulfonchlorides, sulfonic acids, and sulfones. If the heating is omitted, little or no reaction takes place. F. von Heyden Nachfolger[4] found that the —SO_2Cl group took the meta position to the nitro group, there being formed at the same time smaller amounts of the ortho and para derivatives.

Of five experiments made, the one with the following proportions of reacting substances and the conditions here described gave the best results: 100 g. of nitro-*p*-xylene, which had been purified by two distillations with steam and dried over calcium chloride, were added, drop by drop, to 480 g. of chlorosulfonic acid, surrounded by ice. The dark red mixture, placed in a flask, the neck of which was fitted with a calcium chloride tube to protect from atmospheric moisture, was allowed to stand over night. When it was heated on the water bath hydrochloric acid was given off. The heating was continued, with occasional shaking for twelve hours, at the end of which time the evolution of hydrochloric acid gas had practically ceased. When cool the mixture was poured slowly into 2 liters of ice water. This caused the separation of a semi solid brown precipitate which, on standing one hour, solidified in the bottom of the vessel. The solid was filtered off and treated with 1 liter of ether, in which it dissolved, leaving a small amount of tarry residue. The tarry residue was filtered from the solution and the latter dried over calcium chloride. After standing two days the addition of 300 cc. of petroleum ether caused the separation of more tarry matter. After standing five hours longer the solution was filtered from the tarry matter and the calcium chloride. 500 cc. of ether was distilled off and the concentrated solution placed in a beaker, where crystals, which tended to adhere to the sides of the beaker, began to form immediately. The evaporation was continued in a current of dry air until the volume of the solution was reduced to 100 cc. The crystals were filtered off by suction and washed with a mixture of ether and petroleum ether. After recrystallization from ether and petroleum ether they weighed 23 g. One gram of them, recrystallized five times from petroleum ether, gave a constant melting point of 74.5–75.5°. The evaporation of the mother liquor was continued for five days. More crystals separated and at the same time a heavy oil formed in the bottom of the beaker. This second crop of crystals was filtered off and subjected to fractional crystallization. From it was recovered 6.3 g. of the sulfonchloride, m. p. 74.5°, and 10 g. of the more soluble sulfonchloride, mentioned in previous experiments, m. p. 60°. The mother liquor from the second crop of crystals was placed in the ice box and allowed to stand three weeks. It yielded a third crop which weighed 18 g. (crude) and which melted after repeated crystallizations at 60°. The remaining 10 g. of tarry matter, which probably contained some sulfone and *p*-xylenesulfonchloride, did not yield crystals when allowed to stand three weeks at low temperature.

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[1] Jannasch, *Ann.*, 176, 55 (1875).

[2] Armstrong, *Ber.*, 4, 356 (1871).

[3] Dr. F. von Heyden Nachfolger, D. R. P. 89,997; *Frdl.*, 4, 38 (1899).

[4] *Loc. cit.*

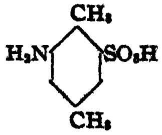
In some of the experiments the crude sulfonchloride, m. p. 74.5°, was recrystallized from pure petroleum ether. While it was more difficultly soluble in pure petroluem ether than in the mixed solvent, fewer crystallizazations were necessary. The tarry impurity, being practically insoluble in petroluem ether, was left on the sides and bottom of the beaker after the sulfonchloride was dissolved.

Determination of Configuration.—In order to determine the configuration of the three crystalline nitrosulfonchlorides, they were hydrolyzed to the corresponding sulfonic acids. These were in turn subjected to the reducing influence of ammonium sulfide in alcoholic solution, or of stannous chloride in hydrochloric acid.

The acid from the sulfonchloride, m. p. 60°, yields, by either method, an aminosulfonic acid of *p*-xylene containing one molecule of water of crystallization. It crystallizes in clusters of very fine white needles which are quite difficultly soluble in cold water. When heated above 200° it begins to char but does not melt even when heated as high as 320°. A temperature of 160° is required for complete dehydration. An analysis gave the following results:

Calc. for $C_8H_{11}O_3NS.H_2O$: H_2O, 8.21%, S, 14.6%; found: H_2O, 8.12%; S, 14.43%.

The properties of the above acid resemble very closely those of the aminosulfonic acid of *p*-xylene prepared by Nolting and Kohn[1] to which they assign the formula



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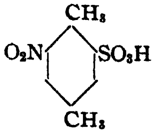
[1] *Ber.*, 19, 143 (1886).

and they are considered identical. The nitrosulfonic acid from which it was prepared must then have the formula,



The nitrosulfonic acid derived from the sulfonchloride melting at 109.5° is not reduced when hydrogen sulfide has been passed through its ammoniacal alcoholic solution for fifteen hours.[1] The unchanged nitrosulfonic acid was identified by means of its barium salt.

Different results were obtained when 5 g. of this acid were treated with three mols (12 g.) of stannous chloride and a slight excess of hydrochloric acid and then warmed for forty-eight hours on the hot plate. The tin was precipitated with hydrogen sulfide, filtered off, and the solution evaporated to dryness on the water bath. The residue was dissolved in water and boiled with barium carbonate. On filtering off the excess of the latter, a considerable amount of *p*-xylidine was found in the filtrate. On standing over night about 0.3 g. of barium sulfate settled out. A small amount of the barium salt of the unchanged nitrosulfonic acid was obtained on evaporation. These results indicate that the nitrosulfonic acid in question, upon being reduced under the conditions given, is at once hydrolyzed to *p*-xylidine and sulfuric acid. Nolting and Kohn[2] mention the occurrence of a small amount of a soluble acid in the mother liquor of 6-amino-1,4-dimethylbenzene-2-sulfonic acid which was oxidizable to *p*-xyloquinone. It is very probable that their soluble acid (?) was simply the hydrochloride of *p*-xylidine which would be readily oxidizable to the quinone.[3] A more thorough study of the conduct of this acid toward reducing agents is now being carried on.

The nitrosulfonic acid from the sulfonchloride melting at 74.5° is readily reduced, either by ammonium sulfide or by stannous chloride and hydrochloric acid. The aminosulfonic acid comes down in clusters of fine prismatic plates or needles, which are slightly less soluble than the aminosulfonic acid already described. The sodium salt crystallizes in small soluble white plates which contain no water of crystallization.

Calc. for $C_8H_{10}O_3NSNa$: Na, 10.32%; found: Na, 10.28% and 10.36%.

The barium salt comes down in readily soluble, long prismatic plates containing seven molecules of water of crystallization.

Calc. for $(C_8H_{10}O_3NS)_2Ba.7H_2O$: H_2O, 19%; Ba, 20.7%; found: H_2O, 19.12% and 19.22%; Ba, 20.48% and 20.36%.

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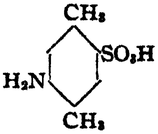
[1] It will be remembered that Frary was unsuccessful in an attempt to reduce this acid with hydrogen sulfide.

[2] *Loc. cit.*

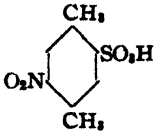
[3] Nolting, *Ber.*, 18, 2667 (1885).

These salts are identical in properties with the sodium and barium salts of 5-amino-1,4-dimethylbenzene-2-sulfonic acid described by Nolting and Kohn.[1] In order to better identify the acid, *p*-xylidine was sulfonated and the barium salt of the acid was decomposed with the calculated amount of sulfuric acid. On filtering off the barium sulfate and evaporating, the aminosulfonic acid came down in well formed needle-like plates which resembled closely in appearance those formed by the reduction of the nitrosulfonic acid.

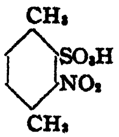
To further verify the identity of the acids, 1 g. of the one resulting from the reduction of the nitrosulfonic acid was oxidized with chromic acid. 0.54 g. of *p*-xyloquinone (phlorone) melting at 124–124.5° was obtained. The acid is then identical with the one which Nolting and Kohn[2] prepared by sulfonating *p*-xylidine and must have the formula



The acid from which it was formed by reduction must then have the formula



Since the nitrosulfonchloride, m. p. 60°, yields, on hydrolysis, 6-nitro-1,4-dimethylbenzene-2-sulfonic acid, and since the nitrosulfonchloride melting at 74.5° yields, on the same treatment, 5-nitro-1,4-dimethylbenzene-2-sulfonic acid, it follows that the nitrosulfonchloride melting at 109.5° must yield, on hydrolysis, 3-nitro-1,4-dimethylbenzene-2-sulfonic acid,



The fact that the acid was not reduced by hydrogen sulfide in ammoniacal alcoholic solution favors this formula, since the protective influence of two groups ortho to the nitro group would naturally be great. It is further shown that the phenyl ester is produced more slowly from the nitrosulfonchloride melting at 109.5° than from either of the other nitrosulfonchlorides. Finally, the very fact that the aminosulfonic acid which is formed by reducing this acid with stannous chloride and hydrochloric acid, is readily hydrolyzed in the presence of acids to *p*-xylidine, favors the assigned formula. Traube[1] has shown that the chloroaminotoluenesulfonic acid, of the formula

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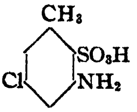
[1] *Ber.*, 19, 141 (1886).

[2] *Loc. cit.*



is readily hydrolyzed in acid solution to the corresponding chloroaminotoluene. It is readily seen that the relative position of the methyl, sulfo- and amino groups are the same in both acids.

Derivatives of 6-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

The Sulfonchloride, $C_6H_2(CH_3)_2NO_2.SO_2Cl$.—This compound is more soluble in a mixture of ether and petroleum ether than either of the other nitrosulfonchlorides of *p*-xylene. It forms regular rhombohedral prisms which show a tendency to form clusters and have a slight amber shade, even after repeated recrystallizations. It is readily soluble in ether, chloroform, carbon tetrachloride, benzene, and carbon disulfide; and less soluble in petroleum ether. When dissolved in a mixture of ether and petroleum ether and evaporated at ordinary temperatures, it tends to settle out as an oil. It is best crystallized from this mixed solvent at a temperature of about 10°. When heated under water it melts to an oil and is slowly hydrolyzed. M. p. 60–61°.

Calc.. Cl, 14.2%, S, 12.82%, N, 5.61%; found Cl, 14.26%, 14.3%; S, 12.66%; N, 5.54%, 5.48%

The Acid, $C_6H_2(CH_3)_2NO_2.SO_2OH.H_2O$.—Ten grams of the sulfonchloride was boiled one and one-half hours with 150 cc. of water under a reflux condenser. The solution was decolorized by boiling with animal charcoal, and evaporated to a thick syrup. On cooling, the acid crystallized out in plates. It was filtered off by suction, washed twice with concentrated hydrochloric acid, in which it was rather insoluble, and dried over sodium hydroxide. The acid was a bitter taste and is very hygroscopic. It is soluble in alcohol, but insoluble in ether, chloroform, carbon tetrachloride, benzene, and carbon disulfide. When heated to 128° it begins to char and does not melt even when heated to 200°. It loses its water of crystallization readily at 100°.

Calc.: H_2O, 7.23%; acid hydrogen, 0.401%; N, 5.62%; found · H_2O, 7.04%, 7.15%; acid hydrogen, 0.392%; N, 5.66%, 5.58%.

The Amide, $C_6H_2(CH_3)_2NO_2SO_2NH_2$.—The sulfonchloride was treated with excess of ammonium hydroxide and heated. It melted to an oil which was soon decomposed, a flocculent precipitate being formed. The mixture was evaporated almost to dryness and the residue washed repeatedly with water. It was then dissolved in alcohol. An equal volume of water was added and the solution set aside to crystallize. The amide comes down in clusters of fine prismatic plates, which are readily soluble in alcohol, ether, and chloroform, but insoluble in water. It melts at 172–173°.

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[1] *Ber.*, **26**, 579 (1893).

Calc.: S, 13.91%; N, 12.17%; found: S, 13.84%; N, 11.81%, 12.16%.

The Anilide, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_5$.—The sulfonchloride was dissolved in carbon tetrachloride and treated with excess of aniline. A precipitate settled at once. The solvent was evaporated, the precipitate washed with hydrochloric acid (1 : 1), dissolved in 10% sodium hydroxide, and reprecipitated with hydrochloric acid. The anilide was filtered off and recrystallized from 50% alcohol. It forms clusters of fine, hard, flat needles which melt at 143–144° and are soluble in alcohol, ether, chloroform, and carbon tetrachloride, but insoluble in water.

Calc.: S, 10.46%; N, 9.07%; found: S, 10.44%; N, 9.05%.

The Phenyl Ester, $C_6H_2(CH_3)_2NO_2SO_3C_6H_5$.—This is best prepared by the Reverdin[1] method: 1 g. of phenol was mixed with an equal weight of pyridine and treated with 2.65 g. of the sulfonchloride. This dissolved with evolution of heat. The solution was warmed on the water bath for five minutes. On cooling, it solidified to a granular mass, which was washed with water and dissolved in hot alcohol. The phenyl ester crystallizes from alcoholic solution in clusters of fine needle-like plates which melt at 117–118°. It is fairly soluble in chloroform, carbon tetrachloride, and benzene, but insoluble in water.

Calc.: S, 10.4%; N, 4.56%; found: S, 10.18%, 10.29%; N, 4.53%.

Sodium Salt, $C_6H_2(CH_3)_2NO_2SO_3Na.2H_2O$.—6-Nitro-1,4-dimethylbenzene-2-sulfonic acid, in solution, was just neutralized with sodium hydroxide solution (litmus). The sodium salt comes down in tree-like clusters of very soluble prismatic plates. It is soluble in hot alcohol. This salt may also be prepared by treating a concentrated solution of the acid with a saturated solution of sodium chloride. It loses its water of crystallization at 108°.

Calc.: H_2O, 12.8%; Na, 7.96%; found: H_2O, 12.69%; Na (as sulfate), 7.79%.

Potassium Salt, $C_6H_2(CH_3)_2NO_2SO_3K.H_2O$.—A solution of the acid was neutralized with 10% potassium hydroxide solution (litmus). On standing, the potassium salt came down from the concentrated solution in clusters, or rosets, of readily soluble, colorless prismatic plates. It is slightly less soluble in alcohol than the sodium salt. It is readily precipitated from a concentrated solution of the acid on the addition of saturated potassium chloride solution.

Calc.: H_2O, 6.24%; K, 14.53%; found: H_2O, 6.34%; K (as sulfate), 14.26%.

Calcium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ca.4H_2O$.—A solution of the acid was boiled with precipitated calcium carbonate. The excess of calcium carbonate was filtered off and the solution evaporated. The salt came down in tree-like clusters of colorless crystals. It is less soluble than the calcium salt of the 3-nitrosulfonic acid and slightly more soluble than that of 5-nitrosulfonic acid. It is slightly soluble in alcohol. A temperature of 200° for ten hours is necessary to effect complete dehydration.

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[1] *Ber.*, 35, 1443 (1902).

Calc.: H_2O, 12.58%; Ca, 7.01%; found: H_2O, 12.45%; Ca (as sulfate), 6.97%.

Barium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ba.2H_2O$.—This salt was prepared from a solution of the acid and barium carbonate after the same manner as the calcium salt. It came down in small, colorless nodules which showed a tendency to adhere to the sides of the beaker. It is slightly soluble in hot alcohol. One of its two molecules of water of crystallization is given up at 150°. A temperature of 200° for six hours is required to drive off the second molecule.

Calc.: H_2O, 5.68%; Ba, 21.69%; found: H_2O, 5.67%; Ba (as sulfate), 21.71%

Silver Salt, $C_6H_2(CH_3)_2NO_2SO_3Ag.H_2O$.—The acid, in solution, was treated with a little more than the calculated amount of silver nitrate, and boiled. The small amount of silver chloride was filtered off and the solution evaporated. The silver salt came down in clusters of fine needle-like plates. It is less soluble than the silver salt of the 3-nitrosulfonic acid and slightly more soluble than the silver salt of the 5-nitrosulfonic acid. It is very slightly soluble in alcohol. When exposed to the light, the crystals slowly decompose and darken in color. They lose their water of crystallization readily when heated above 100°.

Calc.: H_2O, 5.07%; Ag, 30.39%; found: H_2O, 4.91%; Ag (as metal), 30.43%.

Derivatives of 3-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

The Sulfonchloride, $C_6H_2(CH_3)_2NO_2SO_2Cl$.—This crystallizes from a mixture of ether and petroleum ether in clear rhombohedral prisms which melt at 109.5–110.5°. It is less soluble in ether, chloroform, carbon tetrachloride, benzene, and petroleum ether, than either of the isomeric sulfonchlorides. When boiled with water it slowly decomposes, but does not melt.

Calc.: Cl, 14.2%; S, 12.82%; N, 5.61%; found: Cl, 14.32%, 14.26%; S, 12.81%, 12.72%; N, 5.66%.

The Acid, $C_6H_2(CH_3)_2NO_2SO_2OH$.—Ten grams of the sulfonchloride were boiled with 150 cc. of water three hours and twenty minutes under a reflux condenser. On evaporation of the solution to a syrup, the acid crystallized out in clusters of elongated plates. After being dried over sodium hydroxide it melts when heated to 100°. When heated twenty-four hours at 108° it first melts and then hardens and becomes crystalline. When thus dehydrated it melts between 143° and 145° with partial decomposition. Like the 6-nitrosulfonic acid it is less soluble in concentrated hydrochloric acid than in water, fairly readily soluble in alcohol but insoluble in ether, chloroform, carbon tetrachloride, carbon disulfide, benzene and petroleum ether. It is deliquescent.

Calc.: H_2O, 7.23%; acid hydrogen, 0.401%; N, 5.62%; found: H_2O, 7.08%; acid hydrogen, 0.396%; N, 5.57%.

The Amide, $C_6H_2(CH_3)_2NO_2SO_2NH_2$.—One gram of the sulfonchloride was treated with an excess of ammonium hydroxide, warmed, and allowed to stand over night. As this treatment did not decompose the crystals, the mixture was heated three hours on a hot plate. On evaporation, the amide came down in fine flat, shiny needles which, after recrystallization from 50% alcohol, melted at 191–192°. It closely resembles the amide of the 6-nitrosulfonic acid in its solubilities.

Calc.: S, 13.91%; N, 12.17%; found: S, 13.8%, 13.86%; N, 12.21%.

The Anilide, $C_6H_2(CH_3)_2.NO_2.SO_2HNC_6H_5$.—The details of the preparation were the same as those described for the preparation of the anilide of the 6-nitrosulfonic acid. It crystallizes from 50% alcohol in long, flat needles which melt at 181.5–182.5°. It is insoluble in water and slightly less soluble in organic solvents than the anilide previously described. The crystals retain a slight bluish tinge after ten recrystallizations.

Calc.: S, 10.46%; N, 9.07%; found: S, 10.37%; N, 9.06%.

The Phenyl Ester, $C_6H_2(CH_3)_2.NO_2.SO_3C_6H_5$.—The sulfonchloride dissolved more slowly in the pyridine-phenol mixture than did the 6-nitro-1,4-dimethylbenzene-2-sulfonchloride, solution being complete after the mixture had been heated fifteen minutes on the water bath. The ester comes down from alcoholic solution in well formed colorless prisms which show a slight tendency to adhere to the sides of the beaker. It melts sharply between 83° and 83.5° and resembles the phenyl ester of 6-nitro-1,4-dimethylbenzene-2-sulfonic acid as regards its action towards solvents.

Calc.: S, 10.4%; N, 4.56%; found: S, 10.47%; N, 4.51%.

Sodium Salt, $C_6H_2(CH_3)_2.NO_2.SO_3Na.2H_2O$.—This salt comes down in clusters of small, light yellow prismatic plates. Its solubility in water and in alcohol resembles that of the sodium salt of the 6-nitrosulfonic acid. Like this last named compound, it is precipitated when a concentrated solution of the acid is treated with saturated sodium chloride solution. It is dehydrated when heated six hours at 108°.

Calc.: H_2O, 12.8%; Na, 7.96%; found: H_2O, 12.68%; Na, 7.98%.

Potassium Salt, $C_6H_2(CH_3)_2NO_2SO_3K.H_2O$.—This forms tufts of colorless needle-like plates which are slightly less soluble than the crystals of the corresponding sodium salts. It retains its water of crystallization rather persistently, a temperature of 200° being required for complete dehydration.

Calc.: H_2O, 6.24%; K, 14.53%; found: H_2O, 6.02%; K, 14.18%, 14.36%.

Calcium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ca.3H_2O$.—This salt crystallizes in slightly yellow translucent irregular crystals. It is more soluble than the calcium salts of either of the isomeric acids and than the barium salt of this same acid. It is only fairly soluble in alcohol. One of its three molecules of water of crystallization is given off when it is heated three hours at 108°. A temperature of 200° for eight hours is necessary for complete dehydration.

Calc.: H_2O, 9.74%; Ca, 7.24%; found: H_2O, 9.87%; Ca, 7.26%.

Barium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ba.H_2O$.—It forms regular translucent crystals which resemble closely in appearance those of the calcium salt of the acid under consideration. It is more soluble than the barium salts of the isomeric acids. It is dehydrated when heated eight hours at 200°.

Calc.: H_2O, 2.92%; Ba, 22.32%; found: H_2O, 2 84%; Ba, 22.22%.

Silver Salt, $C_6H_2(CH_3)_2NO_2SO_3Ag.H_2O$.—This came down from the concentrated solution in readily soluble plates. It is slightly soluble in alcohol. When exposed to light it darkens more rapidly than either of the other silver salts. It is dehydrated at 108°.

Calc.: H_2O, 5.07%; Ag, 30.39%; found: H_2O, 5.05%, 5.12%; Ag, 30.44%.

Derivatives of 5-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

The Sulfonchloride, $C_6H_2(CH_3)_2NO_2SO_2Cl$.—The sulfonchloride crystallizes from the crude solution in small crystals which show a tendency to adhere to the sides of the beaker. On repeated recrystallization from ether or from a mixture of ether and petroleum ether the crystals take the form of colorless plates with slightly thickened centers. Its solubility in organic solvents is about the same as that of the 3-nitrosulfonchloride. It melts to an oil under hot water by which it is decomposed. When pure it melts at 74.5–75.5°.

Calc.: Cl, 14.2%; S, 12.82%; N, 5.61%; found: Cl, 14 29%; S, 12.8%, 13.03%; N, 5.64%, 5.68%.

The Acid, $C_6H_2(CH_3)_2NO_2SO_2OH.H_2O$.—This was prepared by hydrolyzing the corresponding sulfonchloride in the manner already described. The time necessary for the hydrolysis of 10 g. was two hours and ten minutes. The acid comes down in clusters of needle-like plates from the concentrated solution. It is slightly less soluble than its isomers in water and much less soluble in concentrated hydrochloric acid. When recrystallized from hydrochloric acid and dried over sodium hydroxide it melts with partial decomposition, between 138° and 140°. Like the other acids described it is extremely hygroscopic, has a bitter taste, and loses its water of crystallization at 108°.

Calc.: H_2O, 7.23%; acid hydrogen, 0.401%; N, 5.62%; found: H_2O, 7.22%; acid hydrogen, 0.394%; N, 5.49%, 5.56%.

The Amide, $C_6H_2(CH_3)_2NO_2SO_2NH_2$.—The sulfonchloride was readily decomposed by ammonium hydroxide. The amide comes down from 50% alcohol in fine prismatic plates which may or may not form clusters. When heated, the crystals become opaque at 170° and melt at 197–198°.

Calc.: S, 13.91%; N, 12.17%; found: S, 13.96%; N, 12.18%.

The Anilide, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_5$.—This compound was prepared in the same manner as the anilides already described. It crystallizes out of 50% alcohol, in which it is slightly less soluble than its isomers, in clusters of fine prismatic plates. It has a constant melting point of 130.5–131°.

Calc.: S, 10.46%; N, 9.07%; found. S, 10.36%, 10.42%; N, 9.02%.

The Phenyl Ester, $C_6H_2(CH_3)_2NO_2SO_3C_6H_5$.—This was prepared by the Reverdin method. The sulfonchloride passed into solution immediately with evolution of heat. The ester comes down from alcoholic solution in clusters of light yellow, needle-like plates having a constant melting point of 120°–120.5°.

Calc.: S, 10.4%; N, 4.56%; found: S, 10.47%; N, 4.49%, 4.61%.

Sodium Salt, $C_6H_2(CH_3)_2NO_2SO_3Na.H_2O$.—This forms clusters of flat colorless needles. It is less soluble in water than either of the other sodium salts and rather sparingly soluble in alcohol. It gives up its water of crystallization readily at 108°.

Calc.: H_2O, 6.64%; Na, 8.48%; found: H_2O, 6.75%; Na, 8.33%.

Potassium Salt, $C_6H_2(CH_3)_2NO_2SO_3K.H_2O$.—Prepared in the usual manner, this salt comes down in clusters of shining colorless needle-like plates. It is the least soluble in water and alcohol of any of the sodium or potassium salts studied. It is completely dehydrated when heated six hours at 108°.

Calc.: H_2O, 6.24%; K, 14.53%; found: H_2O, 6.36%, 6.21%; K, 14.12% (puffed), 14.45%.

Calcium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ca.3H_2O$.—This salt was prepared in the usual manner from calcium carbonate and a solution of the acid. It is the least soluble of the calcium salts studied. It comes down in tufts of long, flat, colorless needles which are very sparingly soluble in alcohol. It loses one of its three molecules of water of crystallization when heated four hours at 108°. A temperature of 200° for ten hours is required for complete dehydration.

Calc.: H_2O, 9.74%; Ca, 7.24%; found: H_2O, 9.57%; Ca, 7.16%.

Barium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ba.2H_2O$.—This is the least soluble of the barium salts of the nitrosulfonic acids of *p*-xylene. It comes down in tufts of very fine, colorless needles which show a tendency to adhere to the sides of the beaker. Its solubility in alcohol is about the same as that of the calcium salt of the same acid. It is dehydrated when heated six hours at 200°.

Calc.: H_2O, 5.68%; Ba, 21.69%; found: H_2O, 5.56%; Ba, 21.73%.

Silver Salt, $C_6H_2(CH_3)_2NO_2SO_3Ag.H_2O$.—It forms clusters of long, shining needles. It is considerably less soluble than either of the other silver salts studied and darkens when exposed to the light more slowly than these.

Calc.: H_2O, 5 07%; Ag, 30.39%; found: H_2O, 4.95%; Ag, 30.29%

5-Amino-1,4-dimethylbenzene-2-sulfonic Acid, $C_6H_2(CH_3)_2NH_2SO_2OH$.—The barium and sodium salts of this acid have been studied but there is very little in the literature concerning the properties of the acid itself. As prepared by the reduction of the corresponding nitrosulfonic acid or by the sulfonation of *p*-xylidine and subsequent purification by means of the barium salt, the acid comes down in clusters of fine, prismatic plates or needles. It is somewhat less soluble in water and dilute acids than the 6-aminosulfonic acid. It is quite readily soluble in fairly concentrated sulfuric acid. When heated above 230° it begins to char and does not melt even when heated as high as 300°.

Calc.: S, 15.91%; found: S, 15.62%, 15 74%

The Barium Salt of 6-Amino-1,4-dimethylbenzene-2-sulfonic Acid, $[C_6H_2(CH_3)_2NH_2SO_3]_2Ba.7H_2O$.—This salt comes down in plates which resemble closely in appearance the barium salt of the 5-amino sulfonic acid. They are, however, slightly more soluble. It contains seven molecules of water of crystallization which it loses when heated to 108°.

Calc.: H_2O, 19%; Ba, 20.7%; found: H_2O, 19.28%, 19.18%; Ba, 20.52%, 20.61%.

3. Summary.

1. Nitric acid acts upon the sulfonic acid of *p*-xylene to produce three nitrosulfonic acids. The 6-nitro- and the 3-nitro-1,4-dimethylbenzene-2-sulfonic acid are produced in fairly good yields and in about equal amounts while the 5-nitro-1,4-dimethylbenzene-2-sulfonic acid is produced in very small amounts. It has been shown by Nolting and Geissmann,[1] Lellman,[2] and others that concentrated nitric acid when warmed with *p*-xylene produces, in the main, the 2,6- and the 2,3-dinitro-*p*-xylenes with a very small amount of 2,5-dinitro-*p*-xylene. It would seem, therefore, that the entering nitro group tends to take the meta or ortho position to the sulfonic acid group just as the second nitro group tends to take the meta or ortho position to the first nitro group.

2. The nitrosulfonic acids of *p*-xylene, produced by the nitration of *p*-xylene-sulfonic acid, are best separated by converting them into the sulfonchlorides and crystallizing the latter from a mixture of ether and petroleum ether.[3]

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[1] *Ber.*, 19, 144 (1886).

[2] *Ann.*, 228, 250 (1885).

[3] One separation was made by fractional crystallization of the barium salts. This method gave a somewhat larger yield of the 6-nitro-1,4-dimethylbenzene-2-sulfonic acid than was obtained by the separation of the sulfonchlorides.

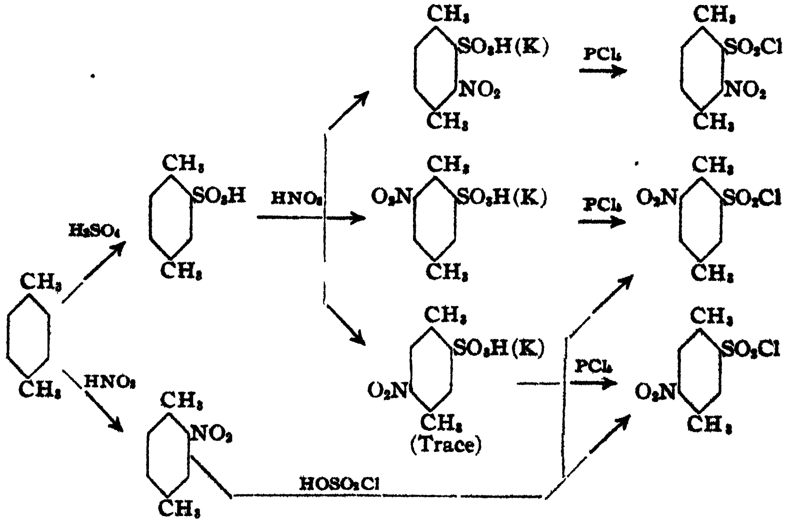
3. Attempts to nitrate the sulfonchloride of *p*-xylene by means of various reagents met with only limited success. In all trials, but one, only one sulfonchloride, and that in small quantities, was produced, *i. e.*, 3-nitro-1,4-dimethylbenzene-2-sulfonchloride. In one case a very small yield of 6-nitro-1-4-dimethylbenzene-2-sulfonchloride was isolated. A rather large excess of nitrosulfuric acid gave the largest yield.

4. Nitro-*p*-xylene is not easily sulfonated. Attempts to sulfonate this compound with sulfuric acid, either at room temperature or on the water bath were not successful.

5. Chlorosulfonic acid acts upon nitro-*p*-xylene at the temperature of boiling water to produce, in about equal amounts, two nitrosulfonchlorides, *i. e.*, 6-nitro- and 5-nitro-1,4-dimethylbenzene-2-sulfonchloride. A considerable amount of tarry matter is also formed. Of these two sulfonchlorides, the last named is the less soluble and may be separated from the other by fractional crystallization from ether and petroleum ether.

6. The configuration of the acids under consideration was determined by reducing them to the corresponding aminosulfonic acids and comparing the properties of these with the properties of the aminosulfonic acids described by Nolting and Kohn.[1] Attempts to reduce 3-nitro-1,4-dimethylbenzene-2-sulfonic acid to the amino acid with hydrogen sulfide in alcoholic solution were not successful. When stannous chloride and hydrochloric acid were used the amino acid formed was at once hydrolyzed.

7. The production of the sulfonchlorides of the three nitrosulfonic acids of *p*-xylene may be briefly represented by the following scheme:



Iowa City, Ia

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[1] *Ber.*, 19, 141 (1886).

[Contribution from the Sheffield Chemical Laboratory of Yale University.]

THE PREPARATION AND PROPERTIES OF SOME HIGHER PHENOLS AND THEIR ETHERS.

By Treat B. Johnson and Edward F. Kohmann

Received April 10, 1914

In a recent publication from this laboratory,[1] was described a practical method of introducing alkyl groups into the benzene nucleus of mono- and polyhydric phenols. It was shown that this can easily be accomplished by reduction of acyl derivatives of phenols (ketone-phenols) to their corresponding alkyl derivatives, by digestion with zinc-amalgam and hydrochloric acid. That the latter reagents may be employed for the reduction of the ketone group was observed by Clemmensen[2] and the method was applied by him successfully for the reduction of the following aliphatic and aliphatic-aromatic ketones, namely, acetophenone, $C_6H_5COCH_3$, ethylphenylketone, $C_6H_5COCH_2CH_3$, propylphenylketone, $C_6H_5COCH_2CH_2CH_3$, methylbenzylketone, $C_6H_5CH_2COCH_3$, methylphenylethylketone, $C_6H_5CH_2CH_2COCH_3$, methyl-α-naphthylketone, $C_{10}H_7$-$COCH_3$, methylnonylketone, $CH_3COC_9H_{13}$, methylheptadecylketone, $CH_3COC_{17}H_{35}$ and stearone, $(C_{17}H_{35})_2CO$. Since the publication of our paper, Clemmensen has contributed two more papers on this reaction and has applied it successfully for the reduction of several varieties of ketones and also of aldehydes.[3] In fact, the results obtained in those cases examined have been so satisfactory, that the reaction may be considered as one of general application.

In our first paper we described the behavior, on reduction, of the lower acyl derivatives of some phenols and their ethers. No aliphatic grouping larger then CH_3CH_2CO- (propionyl) was studied, but in every case examined the reduction was smooth and the yield of alkyl derivative was excellent. In no case did we observe the formation of pinacones. We have found, however, since the completion of this work, that pinacones are formed in some cases.[4] During the progress of our work it became of especial interest to us, for several reasons, to investigate further certain properties of new phenols of the above type, especially those which contain long aliphatic side chains in the benzene nucleus. We had reason to believe, for example, that such phenols would exhibit unique chemical properties and, furthermore, that certain ones might very probably prove to be of immediate, biochemical interest. Several phenol compounds of this character have now been synthesized, and a description of their preparation and properties is recorded in the experimental part of this paper.

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[1] Johnson and Hodge, This Journal, 35, 1014 (1913).

[2] *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 7, 68–80 (1912).

[3] *Ber.*, 46, 1837 (1913); 47, 51 (1914).

[4] These experiments will be discussed in a future paper (T. B. J.).

In September, 1913, the writer announced[1] the fact, that veratrol and myristyl chloride interact smoothly, in the presence of aluminium chloride, forming the ketone—*myristylveratrol* (I). It was also shown

$$C_6H_4(OCH_3)_2 + CH_3(CH_2)_{12}COCl = HCl + CH_3(CH_2)_{12}CO.C_6H_3(OCH_3)_2.$$
(I)

that the latter undergoes reduction, when digested with zinc-amalgam and hydrochloric acid, forming a veratrol derivative, $CH_3(CH_2)_{13}.C_6H_3(OCH_3)_2$, which is isomeric with the dimethyl ether of *hydrourushiol*, $(CH_3O)_2.C_6H_3.C_{14}H_{29}$. The latter substance is a definite crystalline product which is easily obtained by catalytic reduction of the corresponding ether of *urushiol*, a natural component of Japanese lac and first identified by the Japanese investigator, Majima.[2] No conclusion could be drawn at that time, however, regarding the actual identity of the compounds, because we did not have, in our possession, any of Majima's natural substance for comparison. Fortunately, however, soon after the announcement of our work, we received from Professor Majima a sample of his substance and established the fact that the two ethers were only isomeric and not identical. This interesting observation would have been published in THIS JOURNAL several months ago, but for the fact that it has purposely been held back to avoid misunderstandings, and as assurance that we have no intention of interfering with the work of other investigators in this field. Since a reasonable time has now been given for others to conclude their work, it is not necessary for us to delay longer the publication of our results.

In a recent paper entitled: "Eine neue Synthese von höheren Phenolen," Majima and Nakamura[3] have described several alkyl derivatives of veratrol, which were made by the reduction of ketones with zinc-amalgam. Among those synthesized is the tetradecylveratrol, $CH_3(CH_2)_{13}.C_6H_3(OCH_3)_2$, which was described by us. These investigators state that this compound melts at 49–50°, and confirm our observation that it is not identical with the dimethyl ether of hydrourushiol. The latter melts at 38–39°. They apparently failed, however, to recognize an unique property of their synthetical ether. We find that this veratrol is a dimorphic compound and can exist in two modifications, which melt at 37–38.5° and 49°, respectively. Majima and Nakamura were dealing with the stable modification. It is an interesting fact that the melting point of our unstable modification in practically identical with that of the dimethyl ether obtained from *urushiol* (m. p. 38–39°). The unique behavior of our compound is described in the experimental part of this paper.

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[1] Paper presented before Organic Chemistry Section, 48th meeting Am. Chem. Soc , Rochester, N. Y., September 8–12, 1913.

[2] *Ber.*, 40, 4390 (1908); 43, 1418, 3664 (1910); 45, 2427 (1913).

[3] *Ibid.*, 46, 4089 (1914).

We have now investigated the action of zinc-amalgam on the following higher phenol derivatives, which are represented by formulas (II), (III), (IV), (V), (VI) and (VII):

Palmitylethoxybenzene, $C_2H_5OC_6H_4.CO(CH_2)_{14}.CH_3$
(II)

Palmitylveratrol, $(CH_3O)_2.C_6H_3.CO(CH_2)_{14}.CH_3$
(III)

Myristylveratrol, $(CH_3O)_2.C_6H_3.CO(CH_2)_{12}.CH_3$
(IV)

Myristylethoxybenzene, $C_2H_5O.C_6H_4CO(CH_2)_{12}CH_3$
(V)

Dimethylether of myristylhydroquinone, $(CH_3O)_2C_6H_3.CO(CH_2)_{12}CH_3$ (VI)
and myristylphenol, $HO.C_6H_4.CO(CH_2)_{12}CH_3$
(VII)

Every one of these ketones, with the exception of the phenol (VII), underwent reduction smoothly with formation of their corresponding alkyl derivatives. These are represented by formulas (VIII), (IX), (X), (XI) and (XII), respectively.

$C_2H_5O.C_6H_4.(CH_2)_{15}CH_3 \longrightarrow HO.C_6H_4.(CH_2)_{15}CH_3$
(Hexadecylethoxybenzene) (Hexadecylphenol)
(VIII) (XIII)

$(CH_3O)_2.C_6H_3.(CH_2)_{15}CH_3$
(Hexadecylveratrol)
(IX)

$(CH_3O)_2C_6H_3.(CH_2)_{13}CH_3$
(Tetradecylveratrol)
(X)

$C_2H_{50}.C_6H_4(CH_2)_{13}CH_3 \longrightarrow HO.C_6H_4.(CH_2)_{13}CH_3$
(Tetradecylethoxybenzene) (Tetradecylphenol)
(XI) (XIV)

$(CH_{30})_2C_6H_3.(CH_2)_{13}CH_3$
(Dimethylether of tetradecylhydroquinone)
(XII)

The ketone-phenol (VII), was extremely stable and only a trace of the phenol (XIV), was obtained after digesting with zinc-amalgam and hydrochloric acid for 46 hours. The ketone (III) and the corresponding alkyl derivative (X), have been described by Majima and Nakamura.[1] The two ethers, (VIII) and (XI), were easily converted into the corresponding phenols (XIII) and (XIV), by heating with hydriodic acid.

Especially interesting are the facts that the two higher phenols represented by formulas (XIII) and (XIV) are insoluble in aqueous alkali. While it is a very general rule that mono-substituted phenols of this type are soluble in alkali, these compounds, on the other hand, possess practically no acidic properties and approach the aliphatic alcohols in chemical nature. Both phenols, however, react normally with Millon's reagent giving the characteristic test for a phenol group.

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[1] *Loc. cit.*

It is our opinion that this insolubility is not to be explained by the fact that these higher phenols are differently constituted than the lower members of the series. Their neutral character is very probably due to the influence of the positive alkyl chain, in the *para* position of the ring, on the phenolic hydroxyl group. This assumption is supported by the interesting fact that the solubility of the mono substituted phenols, in alkali, apparently grows less as the length of the side chain is increased. An inspection of Table I will reveal these interesting relationships so far as can be brought out from what is known regarding the members of the series. A comparison of other classes of phenol compounds has also revealed similar relationships. A synthesis of the missing representatives of the series would be of interest in order to determine the limit of solubility in alkali.

TABLE I.

Empirical formula.	Phenol compound, $HO.C_6H_4.R$.	Solubility in alkali.
C_6H_6O	Phenol	Soluble
C_7H_8O	(*o*-, *m*-, *p*)-$HO.C_6H_4.CH_3$	Soluble
$C_8H_{10}O$	(*o*-, *m*-, *p*)-$HO.C_6H_4CH_2CH_3$	Soluble
$C_9H_{12}O$	(*o*-, *m*-, *p*)-$HO.C_6H_4(CH_2)_2CH_3$	Soluble
	(*o*-, *m*-, *p*)-$HO.C_6H_4.CH(CH_3)_2$	Soluble
$C_{10}H_{14}O$	(*p*)-$HO.C_6H_4.CH(CH_3)(C_2H_5)$	Soluble
	(*p*)-$HO.C_6H_4.C(CH_3)_3$	Soluble
$C_{11}H_{16}O$	(*p*)-$HO.C_6H_4.(CH_2)_2CH(CH_3)_2$	Soluble
$C_{12}H_{18}O$	None described	
$C_{13}H_{20}O$	$HO.C_6H_4.CH(C_3H_7)_2$	?
$C_{14}H_{22}O$	$HO.C_6H_4CH(CH_3)(CH_2)_5CH_3$	?
$C_{15}H_{24}O$	Cynanchocerin or cynanchin[1](?)	Insoluble
$C_{16}H_{26}O$	None described	
$C_{17}H_{28}O$	None described	
$C_{18}H_{30}O$	None described	
$C_{19}H_{32}O$	None described	
$C_{20}H_{34}O$	(*p*)-$HO.C_6H_4.(CH_2)_{13}.CH_3$	Insoluble
$C_{21}H_{36}O$	None described	
$C_{22}H_{38}O$	(*p*)-$HO.C_6H_4(CH_2)_{15}.CH_3$	Insoluble
$C_{23}H_{40}O$	None described	

The variations in degree of acidity of the phenolic group OH— in this series in undoubtedly due to the same influence as that observed by Solonina[2] in the case of alkali soluble derivatives of benzene sulfonamide. For example, he found that only the lower mono-alkyl substitution products of this sulfonamide, $C_6H_5SO_2NHR$, possess strong acidic properties.

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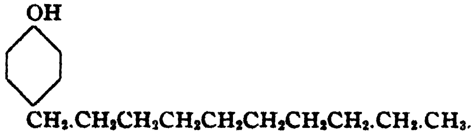
[1] Hesse, *Ann.*, 182, 163; 192, 183.

[2] *Chem. Centr.*, 2, 867 (1899).

If alkyl groups containing more than six carbon atoms were substituted in the amide grouping the $SO_2.NH$ group lost its acidic properties and the resulting alkyl amides were absolutely insoluble in alkalies. Benzenesulfonheptylamide, $C_6H_5SO_2NH.(CH_2)_6CH_3$, benzene-sulfoncamphylamide $C_6H_5SO_2NH.C_{10}H_{17}$ and their corresponding *p*-bromobenzenesulfon- and *m*-nitrobenzenesulfonderivatives are examples of insoluble sulfonamides obtained. The benzenesulfonderivative of 2-aminoundecan was also insoluble. In other words, these higher alkyl groups apparently exert the same influence here on the acidity of the —$SO_2.NH$— grouping as that of the corresponding radicals on the acid OH group in the above phenols.

Hesse[1] observed that *cynanchocerin* and *cynanchin*, two isomeric substances of unknown constitution, which he obtained from the sap of swallow-wort (*Cynanchum acutum*), are both insoluble in alkali and interact with sulfuric acid giving violet solutions (röthlich violett). It is of especial interest, now, to note that these two compounds are listed in Beilstein's Handbuch under phenols and the conclusion made that they are phenol ethers because of their insolubility in alkali. From what has already been shown it is not improbable that these substances may be true phenols, but contain long side chains which neutralize the acidic properties of the hydroxyl group.



Our investigations on phenols will be continued.

Experimental Part.

1,4-Hexadecylethoxybenzene. $C_2H_5O.C_6H_4.(CH_2)_{15}.CH_3$.—This benzene derivative was prepared by the reduction of 1,4-palmitylethoxybenzene.[2] Eleven and four-tenths grams of the ketone, an excess of amalgamated zinc and 300 cc. of hydrochloric acid (1 vol. concentrated acid to 2 vols. of water) were digested on a sand bath for about 15 hours, when the reduction was apparently complete and 11.5 g. of the crude ether were obtained. After crystallizing from alcohol this product melted at 40–54°, indicating that it was a mixture of the ketone and reduced ether. The mixture was again digested with zinc-amalgam for 8 hours, a little alcohol being added to aid solution of the ketone. After this second treatment we obtained the ether as a colorless, cystalline substance which separated from hot alcohol in globules of oil that immediately solidified on cooling. The ether melted at 43–45° to a clear oil. The yield of purified material was 6.5 g.

Calc. for $C_{24}H_{42}O$: C, 83.15; H, 12.2; found. C, 82.19; H, 11.85, 11.83.

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[1] *Loc. cit.*

[2] Krafft, *Ber.*, 21, 2270 (1888)

p-Hexadecylphenol, $CH_3(CH_2)_{15}.C_6H_4.OH$.—This phenol was obtained by heating the above ether with hydriodic acid in a pressure tube at 150–180°. It was insoluble in water and was purified by crystallization from petroleum ether. It separated from this solvent in needles which melted at 78–79°. The phenol crystallizes from alcohol in clusters of radiating prisms. This phenol is absolutely insoluble in sodium hydroxide solution. It gives Millon's test.

Calc. for $C_{22}H_{38}O$: C, 82.9; H, 12.0; found: C, 82.26; H, 11.84.

This compound has previously been described by Krafft,[1] and was prepared by fusion of the *p*-sulfonic acid derivative of cetylbenzene, $CH_3(CH_2)_{15}.C_6H_4.SO_3H$, with potassium hydroxide at 250°. He assigned the temperature of 77.5° as its melting point. Later Krafft and Göttig[2] described its ethylether (above), which was prepared by heating the phenol in alcoholic potash with methyl iodide. They found this to melt at 43–44°, practically the same temperature as observed by us (43–45°).

Palmitylveratrol, $CH_3(CH_2)_{14}CO.C_6H_3(OCH_3)_2$.—This ketone has recently been described by Majima and Nakamura.[3] We prepared it by application of Friedel and Crafts' reaction with veratrol and palmitylchloride in carbon disulfide solution. It was purified by distillation under diminished pressure and recrystallization from alcohol. It melted at 78–79°. Majima observed that his product melted at 79–80°.

Calc. for $C_{24}H_{40}O_3$: C, 76.53, H, 10 71, found C, 76.43, H, 10 73

Hexadecylveratrol, $CH_3(CH_2)_{15}.C_6H_3(OCH_3)_2$.—This ether was formed quantitatively by reduction of the above ketone with zinc-amalgam and hydrochloric acid. It crystallized from alcohol in plates which melted at 55° to an oil.

Calc. for $C_{24}H_{42}O_2$. C, 79.48; H, 11.68; found: C, 79.90; H, 11.73

Myristylveratrol, $CH_3(CH_2)_{12}CO.C_6H_3(OCH_3)_2$.—Majima and Nakamura[3] prepared this ketone by the action of myristyl chloride on veratrol in the presence of aluminium chloride. No diluent was used. From 10.7 g. of the acid chloride and 17 g. of the veratrol they obtained 3.5 g. of the pure ketone. We find that a much better yield of the ketone can be obtained if the reaction is applied in the presence of petroleum ether. Our procedure was as follows: Twenty-seven grams of the acid chloride were dissolved in 25 g. of petroleum ether and 15 g. of aluminium chloride suspended in the solution. Fifteen grams of veratrol were then added in portions, the mixture being cooled to —5°. On adding the veratrol under these conditions, a precipitate was obtained, but there was no appreciable amount of hydrochloric acid generated. After all the veratrol had been added, 50 cc. of petroleum ether were then added and the mixture allowed to stand at a temperature of 30–40° for fully 21–22 hours. Under these conditions the reaction proceeded smoothly, and hydrochloric acid gas was copiously evolved. In order to isolate the ketone, the reaction mixture, which had separated in two layers, was poured into a large volume of cold water, when a double aluminium chloride compound separated in the form of a grayish brown solid. This was then transferred to hydrochloric acid and the mixture warmed on the steam bath when the ketone was finally obtained as an oil which soon solidified on cooling. The yield of crude material was 40 g., or practically a theoretical yield. The ketone was purified by crystallization from alcohol and separated, on cooling, in aggregates of colorless needles melting at 73–75°. The yield of purified ketone was 32 g. A red color is produced when this ketone is mixed with concentrated sulfuric acid.

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[1] *Ber.*, 19, 2984 (1886).

[2] *Ibid.*, 21, 3181 (1888).

[3] *Loc. cit.*

Calc. for $C_{22}H_{36}O_3$ C, 75.79, H, 10.19; found C, 75.48; H, 10.12.

Tetradecylveratrol, $CH_3(CH_2)_{13}.C_6H_3(OCH_3)_2$.—This ether has recently been described by Majima,[1] and was obtained by catalytic reduction of tetradecenylveratrol and also by reducing the above ketone with zinc-amalgam. Only 2.5 g. of the ketone, however, were reduced by the latter method and no statement is made regarding the yield obtained.

We have now prepared this same ether by reducing the ketone with zinc-amalgam and hydrochloric acid and have obtained some interesting data which contribute to our knowledge of the properties of this compound.

Eleven grams of the above ketone and 25 g. of amalgamated zinc were suspended in 100 cc. of hydrochloric acid (1 vol. of concentrated hydrochloric acid to 2 vol. of water) and the mixture digested for 5 hours. Under these conditions the ketone had undergone practically no reduction and melted at 71.5–73°. Twenty-five grams of amalgam and 25 cc. of concentrated hydrochloric acid were then added and the digestion continued for 9 hours. After this treatment, the ketone was still only partially reduced and melted at 60–67°.

One hundred grams of zinc-amalgam and 150 cc. of hydrochloric acid were then added and the digestion continued for 7 hours longer when the melting point had been lowered to 45°. This melting point, however, was not sharp, the product beginning to melt as low as 39°. Therefore, 30 cc. of concentrated hydrochloric acid were added and the reduction continued for 6.5 hours when the reaction was apparently complete. The compound was purified by crystallization from boiling alcohol. It separated in prismatic crystals, on cooling, which melted at 47–49°. Majima and Nakamura[1] give 49–50° as the melting point. We found, however, that this compound can be made to melt at a much lower temperature. In fact, it is apparently capable of existing in two modifications—one melting at 37–38.5°, and the other melting at 47–49°. The lower modification slowly undergoes transformation into the higher melting isomer at ordinary temperature. Especially striking is the change of the lower melting form into the higher. If the compound is melted in a capillary tube and the latter suddenly cooled by plunging into ice water, it then melts sharply at 37–38.5° to an oil. Almost immediately, however, after this change, crystals begin to appear in the fluid and finally the whole mass solidifies and then melts at 47–49°. This lower melting modification was also obtained by crystallization from alcohol. It is an interesting fact that the dimethylether of hydrourushiol[1] melts at 38–39°, or practically at the same temperature as the melting point of our unstable modification.

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[1] *Loc. cit.*

Calc. for $C_{22}H_{38}O_2$· C, 78.95; H, 11.46; found: C, 78.67; H, 11.18

1,4-Myristylethoxybenzene, $CH_3(CH_2)_{12}CO.C_6H_4.OC_2H_5$.—This ketone was prepared by application of Friedel and Crafts' reaction with 52 g. of myristyl chloride and 100 g. of phenetol in the presence of 72 g. of aluminium chloride. After heating for two days at 60–70° the mixture was then poured while warm into warm, dilute hydrochloric acid and the crude ketone extracted with ether. After drying over calcium chloride, the ketone was subjected to distillation under diminished pressure and that fraction saved which boiled from 260–320° at 27–35 mm. This weighed 29 g. and was purified by crystallization from alcohol. It separated from this solvent in colorless blocks which melted at 66–67° to an oil.

Calc. for $C_{22}H_{36}O_2$. C, 79.44; H, 10.92; found: C, 79.02; H, 10.72.

1,4-Tetradecylethoxybenzene, $CH_3(CH_2)_{13}.C_6H_4.OC_2H_5$.—This compound was easily obtained by reduction of the above ketone with zinc amalgam and hydrochloric acid. It was purified by crystallization from alcohol and melted at 36–36.5° to an oil.

Calc. for $C_{22}H_{38}O$. C, 82.94; H, 12.03; found· C, 82.52; H, 11.83

1,4-Tetradecylphenol, $CH_3(CH_2)_{13}.C_6H_4.OH$.—This phenol was obtained by heating the ethyl ether (above) with glacial acetic acid, saturated at 0° with hydrochloric acid, for 2–3 hours at 150–160°. It was insoluble in water and was purified by crystallization from petroleum ether and separated in stout prisms, which melted at 73–74°. The phenol is insoluble in aqueous sodium hydroxide solution. It gives Millon's test.

Calc. for $C_{20}H_{34}O$: C, 82.67; H, 11.81; found: C, 82.25; H, 11.87.

The phenol is also formed smoothly by heating the ether in a pressure tube with hydriodic acid and a trace of phosphorus at 155–156°.

1,4-Myristylphenol, $CH_3(CH_2)_{12}CO.C_6H_4.OH$.—Twenty-five grams of myristyl chloride and 13 g. of phenetol were dissolved in 150 cc. of dry carbon disulfide. Thirty-five grams of aluminium chloride were then added, in small portions at a time (2 g.) to avoid too violent action, and the solution finally heated to boiling for 5 hours. The mixture was then poured into dilute hydrochloric acid and finally heated on the steam bath to expel the carbon bisulfide. The ketophenol was then obtained as a heavy, black oil which dissolved immediately in cold dilute sodium hydroxide solution. In order to purify the phenol for analysis the alkaline solution was digested with bone coal and the phenol then precipitated by addition of hydrochloric acid. It separated as a brown powder and was purified further by crystallization from a large volume of petroleum ether. It separated in the form of a pink powder and melted at 74–74.5° to an oil. The yield was poor.

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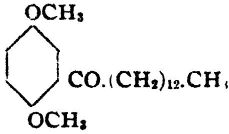
[1] Majima, *Ber.*, 45, 2729 (1912).

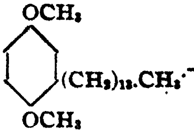
Calc. for $C_{20}H_{32}O_2$: C, 78.86; H, 10.60; found, C, 78.96; H, 10.81

An attempt to reduce this ketone to the corresponding tetradecylphenol with zinc-amalgam was unsuccessful. Only a mere trace of this phenol was obtained after digesting 11 g. of the ketone with amalgam and hydrochloric acid for 46 hours. The reduced product was easily separated from the ketone by treatment of the raw reduction product with dilute sodium hydroxide solution. The tetradecylphenol was insoluble in the alkali and was identified by its melting point (73–74°).

Dimethylether of Myristylhydroquinone, 

—This compound was easily obtained by application of Friedel and Crafts' reaction with 15 g. of hydroquinone dimethylether, 26 g. of myristyl chloride and 16 g. of aluminium chloride. Petroleum ether was used as a diluent. The reaction was extremely smooth and the yield of crude material was 37 g. The ketone was purified by crystallization from alcohol and separated in plates, which melted at 51–52° to an oil. The compound was insoluble in aqueous sodium hydroxide solution and did not give Millon's test. It dissolved, however, in a cold alcoholic solution of sodium hydroxide while, on the other hand, the reduction product (below) was insoluble in this same solvent.

Calc. for $C_{22}H_{36}O_3$: C, 75.79; H, 10.42; found: C, 75.58; H, 10.83.

Dimethylether of Tetradecylhydroquinone, 

—This compound was obtained by reduction of the above ketone with amalgamated zinc and hydrochloric acid. It is very soluble in cold ether, petroleum ether and difficultly soluble in cold alcohol. The compound boiled at 260–275° under 25–35 mm. pressure and crystallized from petroleum ether in aggregates of short needles which melted at 65° to an oil.

Calc. for $C_{22}H_{38}O_2$: C, 78.94; H, 11.45; found: C, 78.52; H, 11.10.

The Action of Nitric Acid on Tetradecylveratrol.—This ether apparently does not interact smoothly with nitric acid. Two grams of the veratrol were suspended in 12 cc. of concentrated nitric acid (sp. gr. 1.42) and the acid warmed sufficiently to melt the ether. This was then left in contact with the acid for about 10 minutes and then washed free from acid by pouring into cold water. The nitro compound was finally purified as follows: It was extracted with ether and dried over calcium chloride. After spontaneous evaporation of the ether, the nitro compound was purified further by crystallization from petroleum ether when it separated in the form of flakes which melted at 91–93°. The yield was small. A nitrogen determination agreed with the calculated value for a mononitro derivative—$CH_3(CH_2)_{13}.C_6H_2(NO_2)(OCH_3)_2$.

Calc. for $C_{22}H_{37}O_4N$· N, 3.69; found: N, 3.8.

Majima and Nakamura[1] observed that the mononitro derivative of the dimethylether of hydrourushiol melts at 72–73°.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

ELECTROMERS AND STEREOMERS WITH POSITIVE AND NEGATIVE HYDROXYL.

BY LAUDER WILLIAM JONES.

Received March 9, 1914.

Although hydroxylamine is one of the simplest inorganic compounds containing nitrogen, it has not escaped speculative controversy concerning the structural formula best suited to represent it. Two formulas have been proposed:

$$\underset{\text{(I)}}{H_2N—OH} \qquad\qquad \underset{\text{(II)}}{H_3N=O}$$

Many of its reactions in organic chemistry, as well as some of its physical constants,[2] seemed to justify the formula which the name, hydroxylamine, implies. Some of the reactions, however, and especially the dual role which hydroxylamine plays as an oxidizing agent and as a reducing agent, have inclined other investigators to support the second formula.

One of the earliest statements of this view was made by Kolotow,[3] who heated hydroxylamine with ammonia at 100°, but could not find a trace of hydrazine. From this vague experiment, he concluded that hydroxylamine did not react as a hydroxyl compound, and that the formula, $H_3N=O$ was consequently the more probable. Haber[4] found that hydroxylamine in alkaline solution oxidized ferrous hydroxide to ferric hydroxide, and was itself reduced to ammonia; while an acid solution, containing a hydroxylamine salt, reduced ferric salts to ferrous salts, with the evolution of a gas which was almost pure nitrous oxide. His conclusion was that the reactions of hydroxylamine could be interpreted best by assigning two different formulas to it, *viz.*, formula (I), or the salt, $NH_3(OH)Cl$, in acid solution, and formula (II) in alkaline solution.

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[1] *Loc. cit.*

[2] Brühl preferred the formula, $H_2N—OH$, as more consistent with his spectrochemical findings. *Ber.*, 32, 566 (1899).

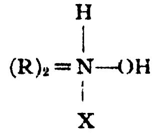
[3] Kolotow, *Ber.*, 26, 761 (1893).

[4] Haber, *Ibid.*, 29, 2444 (1896).

In these disputed relations, as in other cases of a similar character, the opinion gradually emerged that hydroxylamine must be placed among the ever increasing number of tautomeric substances. The deportment of hydroxylamine with various alkylating and acylating agents shows all of the earmarks of the well known Protean reactions so commonly met with in the study of tautomeric substances. In my opinion, the experimental evidence is sufficient, not only to establish a tautomeric relationship in the ordinary structural sense, but also, as will be shown later, to confirm the belief that hydroxylamine and its derivative, in many of their reactions, behave tautomerically in the electronic sense[1] as well.

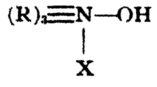
Structural Tautomerism of Hydroxylamine Derivatives.

The experiments of Dunstan and Goulding[2] suggested structural tautomerism, since they showed conclusively that direct alkylation of hydroxylamine led, in all cases, to salts of β- or N-alkyl hydroxylamines of the following types:



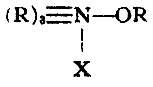
$(R)_2{=}\overset{\displaystyle H}{\underset{\displaystyle X}{N}}{-}OH$

(A)



$(R)_3{\equiv}\underset{\displaystyle X}{N}{-}OH$

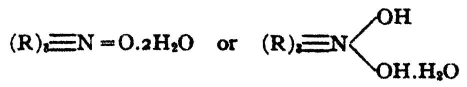
(B)



$(R)_3{\equiv}\underset{\displaystyle X}{N}{-}OR$

(C)

By the action of alkalies upon compounds of type (A), β-dialkyl hydroxylamines, $(R)_2N{-}OH$, were obtained. When compounds of type (B) were treated with silver oxide and water, they gave hydrated amine oxides,



$$(R)_3{\equiv}N{=}O.2H_2O \quad \text{or} \quad (R)_3{\equiv}N\begin{matrix}\diagup OH \\ \diagdown OH.H_2O\end{matrix}$$

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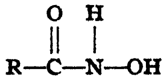
[1] Fry, *Z. physik. Chem.*, **76**, 391 (1911); Jones, *Am. Chem. J.*, **48**, 26 (1912); Bray and Branch, THIS JOURNAL, **35**, 1440 (1913); Fry, *Ibid.*, **36**, 265 (1914). W. A. Noyes (*Ibid.*, **35**, 767 (1913)) has given some experimental evidence which seems to indicate the existence of a nitro-nitrogen trichloride, $N\overset{+}{\underset{+}{+}}(Cl^-)_3$, differing from the ordinary ammono-nitrogen trichloride, $N{\equiv}(Cl^+)_3$. The possibility of ammonia dissociating ionically to give $N{\equiv}$ and $N\overset{+}{\underset{+}{+}}$, with positive hydrogen in one case and negative hydrogen in the other, was assumed by Noyes in an early article (THIS JOURNAL, **23**, 430 (1901)).

[2] Dunstan and Goulding, *J. Chem. Soc.*, **69**, 839 (1896); **75**, 1005 (1899).

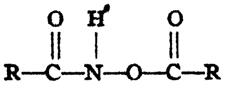
By careful dehydration of these substances, Meisenheimer[1] prepared anhydrous amine oxides, $(R)_3N{=}O$, which could be sublimed *in vacuo* to give solid crystalline compounds. The structural formulas assigned to them were confirmed by the fact that they all gave tertiary amines upon reduction, and that tertiary amines, when treated with hydrogen peroxide, were changed into amine oxides. Halogen alkyls reacted with the amine oxides to form derivatives of type (C). These experiments show that compounds obtained by the direct alkylation of hydroxylamine must be referred to the formula, $H_3N{=}O$.

When, however, halogen acyls or acid anhydrides react with hydroxylamine, the first acyl always replaces a hydrogen atom in the β- or N-position (I); but the second acyl group invariably assumes the α- or O-position (II).



$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-OH$$

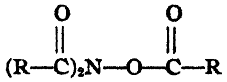
(I)



$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-O-\overset{\overset{O}{\|}}{C}-R$$

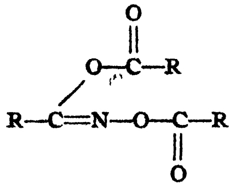
(II)

The third acyl group may substitute the remaining hydrogen atom in the β- or N-position,[2] or it may react with the hydroximic form to give an oxygen-acyl derivative.



$$(R-\overset{\overset{O}{\|}}{C})_2N-O-\overset{\overset{O}{\|}}{C}-R$$

or



From these observations, the conclusion may be drawn that hydroxylamine reacts with acylating agents as if it had the formula, $H_2N{-}OH$. In fact, it was reactions of this particular character which induced Lossen[3] to decide that "the three hydrogen atoms of hydroxylamine were not equivalent,"[4] and to choose the formula $H_2N{-}OH$ in preference to the formula $H_3N{=}O$. If the action of alkylating agents had been unravelled first, we should probably have used the formula $H_3N{=}O$, instead of formula (I).

In addition to these instances, the reactions of alkylating agents with aldoximes and with ketoximes furnish further evidence of a similar character. With compounds of these two classes; it frequently happens that one and the same reagent gives two types of alkyl derivatives during the same reaction.[5]

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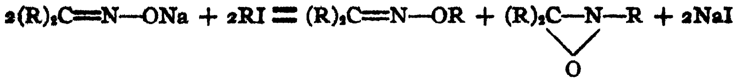
[1] Meisenheimer, *Ann.*, 385, 117 (1901).

[2] Jones, *Am. Chem. J.*, 20, 15 (1898); 48, 19 (1912).

[3] Lossen, *Ann.*, 161, 347 (1872); 175, 271 (1874); 186, 1 (1877); 252, 170 (1889); *Ber.*, 17, 1587 (1884).

[4] Lossen, *Loc. cit.*

[5] Beckmann, *Ber.*, 22, 1536 (1889).



$$2(R)_2C{=}N{-}ONa + 2RI = (R)_2C{=}N{-}OR + (R)_2\underset{\diagdown\, O\, \diagup}{C{-}N}{-}R + 2NaI$$

The Oxidation and Reduction of Hydroxylamine and Its Derivatives.

Before the evidence in favor of tautomerism in the electronic sense is presented, attention may be called to the fact that the controversy regarding a formula for hydroxylamine is based upon arguments which are very closely allied to those advanced for hydrogen peroxide. In fact, a number of chemists have emphasized the striking similarity in behavior of these two substances. Both compounds act as oxidizing agents and as reducing agents; and, to explain these contrasting reactions, analogous structural formulas have been proposed for each.

Hydroxylamine: $H_2N{-}OH$ and $H_3N{=}O$

Hydrogen peroxide: $HO{-}OH$ and $H_2O{=}O$

Wagner[1] called attention to this resemblance, and stated that hydroxylamine might be regarded as hydrogen peroxide in which one hydroxyl group had been replaced by the amido group. From this point of view, hydroxylamine would be the *amide* of hydrogen peroxide, and hydrazine would be its diamide

$$H{-}O{-}OH \qquad H{-}O{-}NH_2 \qquad H_2N{-}{-}NH_2.$$

Hydroxylamine and its derivatives are so prone to engage in reactions involving either intramolecular or intermolecular oxidization and reduction that there is no difficulty in finding siutable cases to illustrate this behavior; a few chosen at random will suffice.

In the first place, it has been shown that the instability of hydroxylamine itself may be explained by changes involving mutual oxidation and reduction. The reactions are expressed approximately by the following equations:

$$3NH_3O = N_2 + NH_3 + 3H_2O \text{ (major)}$$
$$4NH_3O = N_2O + 2NH_3 + 3H_2O \text{ (minor)}$$

The β-disubstituted hydroxylamines, $(R)_2N{-}OH$, form a class of compounds which seem to lie close to the border line of instability. By very slight changes in the physical or chemical conditions, they generally decompose to give products which would be expected to result by a process of intramolecular oxidation.[2] Thus, Walder[3] found that β-dibenzyl hydroxylamine, $(C_7H_7)_2N.OH$, in the presence of acetyl chloride, or even with hydrogen chloride and acetic acid (Beckmann's mixture), gave chiefly benzaldehyde and benzylamine. Dunstan and Goulding[1] stated that β-diethylhydroxylamine, when heated, gave acetaldehyde and ethylamine.

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[1] Wagner, *Z. Russ. phys. chem. Soc.*, **30**, 721 (1899); C. B., 1, 244 (1899); see also Angeli, *Chem. Zentr.*, 11, 804 (1910); Stieglitz and Curme, *Ber.*, **49**, 1011 (1913); Stieglitz, THIS JOURNAL, **36**, 282 (1914) note.

[2] Victor Meyer, *Ber.*, **19**, 1629 (1886) note: An electronic interpretation was given by Jones, *Am. Chem. J.*, **49**, 422 (1913).

[3] Walder, *Ber.*, **19**, 1629, 3287 (1886); Behrend and Leuchs, *Ann.*, **257**, 233 (1890).

$$(C_2H_5)_2N—OH = CH_3CHO + C_2H_5—NH_2.$$

Bewad[2] studied the action of oxidizing agents upon many β-dialkylhydroxylamines. With β-ethyl-*sec.*-amylhydroxylamine, he obtained acetaldehyde, *sec.*-amylamine, diethylketone, ethylamine, with some ammonia and ethyl-*sec.*-amylamine. An interesting statement concerning the quantitative relationship existing between the amount of oxidation effected by the oxidizing agent and that due to intramolecular oxidation caused by the alkylhydroxylamine itself is found in Bewad's article. He said, "The oxygen from the hydroxylamine derivative participated in the reaction is such a way that the share of oxidation alloted to the oxidizing agent was *very much less* than that produced by the alkylhydroxylamine itself."

It is noteworthy that similar changes have been reported by Berg[3] in the study of dialkylchloroamines, $(R)_2N—Cl$. Thus, ethyl-isoamylchloramine, $(C_2H_5)(C_5H_{11})N—Cl$, upon treatment with alcoholic potash and then with acids, gave acetaldehyde, isoamylamine, isovalericaldehyde, and ethylamine. It will be observed that this reaction is strikingly like the one which has been shown to occur with β-ethyl-*sec.*-amylhydroxylamine, $(C_2H_5)(C_5H_{11})N—OH$.

There are many reasons for believing that this analogy is not superficial, but *highly significant;* and that the mutual oxidation and reduction of dialkylchloroamines and of β-disubstituted hydroxylamines have a similar underlying cause. The fact that the chlorine atom[4] in chloroamines must be considered as positive (Cl^+) in character suggests the possibility, and even the probability, that the hydroxyl group in β-dialkyl hydroxylamines may be positive[5] (HO^+) also.

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[1] Dunstan and Goulding, *J. Chem. Soc.*, 75, 793 (1899).

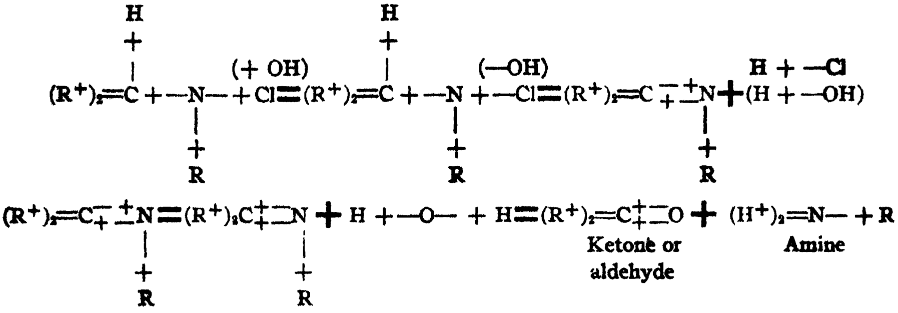
[2] Bewad, *J. prakt. Chem.*, 63, 193 (1901).

[3] Berg, *Bull. soc. chim.*, [3] 17, 297 (1897); Jones, *Am. Chem. J.*, 49, 426 (1913).

[4] Two atomic weights of iodine are liberated for every atomic weight of chlorine in the chloroamine. Seliwanow, *Ber.*, 25, 3617 (1892); Noyes and Lyon, THIS JOURNAL, 23, 463 (1901); Noyes, *Ibid.*, 35, 767 (1913); Stieglitz, *Ibid.*, 23, 769 (1901); 29, 51 (1903), etc.

[5] Stieglitz, THIS JOURNAL, 36, 288 (1914) in a foot-note makes the following statement concerning positive hydroxyl: "The similar behavior of hydroxylamines and halogen amines, of hydroyxlamine and hydrogen peroxide, still more the fundamental similarity existing between hydroxylamines and ammonia and between their salts, and, above all, the fact that, as far as the writer is aware, no hydroxylamine derivative has been found to exchange hydroxyl for halogen by treatment with halogen acid or phosphorus halides are facts on which the writer's views are based. (According to a later private communication from Dr. Jones he has now reached the same conclusion on this question and has discovered further evidence supporting it.")

From this point of view, the analogy between these two reactions may be expressed by the following equations:

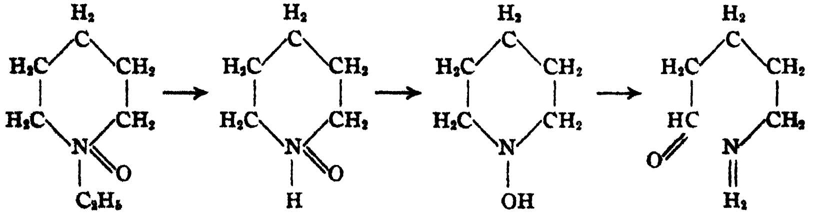


$$(R^+)_2{=}\overset{\overset{H}{+}}{\underset{}{C}}+\!-\!\underset{\underset{R}{+}}{N}\!-\!+Cl\overset{(+OH)}{\equiv}(R^+)_2{=}\overset{\overset{H}{+}}{C}+\!-\!\underset{\underset{R}{+}}{N}+\!-\!Cl\overset{(-OH)}{\equiv}(R^+)_2{=}C\mp\pm\underset{\underset{R}{+}}{N}+\overset{H+-Cl}{(H+-OH)}$$

$$(R^+)_2{=}C\mp\pm\underset{\underset{R}{+}}{N}\equiv(R^+)_2C\ddagger\!-\!\underset{\underset{R}{+}}{N}+H+\!-\!O\!-\!+H\equiv\underset{\text{Ketone or aldehyde}}{(R^+)_2{=}C\ddagger\!-\!O}+\underset{\text{Amine}}{(H^+)_2{=}N-}+R$$

More conclusive evidence in support of this assumption will be presented later in this article.

The amine oxides, $R_3N{=}O$, furnish many interesting illustrations of intramolecular and intermolecular oxidation. Merling,[1] and later Wernick and Wolffenstein,[2] prepared members of this class of compounds by oxidizing *N*-alkylpiperidines and similar compounds with hydrogen peroxide. *N*-methylpiperidine oxide, $C_5H_{10}N({=}O)CH_3$, showed the surprising property of parting with its oxygen when a stream of hydrogen chloride was passed through it, or when it was gently heated. *N*-methylpiperidine was regenerated almost quantitatively. The corresponding ethyl derivative, when heated, decomposed in two ways: (*a*) to give *N*-ethylpiperidine and oxygen; (*b*) to give ethylene and δ-aminovalerianic aldehyde. Since δ-aminovalerianic aldehyde is formed by the action of hydrogen peroxide upon piperidine, it may be assumed that ethylene was produced first, and that the amino aldehyde resulted by a process of intramolecular oxidation resembling that described above in the case of β-dialkyl hydroxylamines.



Very similar reactions have been noted by Dunstan and Goulding,[3] by Mamlock and Wolffenstein[4] and by Meisenheimer[5] in the study of simpler amine oxides. Thus, trimethylamine oxide readily decomposed in two ways: (*a*) to give trimethylamine and oxygen gas; (*b*) to give formaldehyde and dimethylamine.

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[1] Merling, *Ber.*, 25, 3123 (1892).

[2] Wernick and Wolffenstein, *Ber.*, 31, 1553 (1898).

[3] Dunstan and Goulding, *J. Chem. Soc.*, 75, 799, 1004 (1899).

[4] Mamlock and Wolffenstein, *Ber.*, 33, 159 (1900); 34, 2499 (1901)

[5] Meisenheimer, *Ann.*, 385, 117 (1911); 396, 75 (1912); 397, 273 (1912); 399, 371 (1913); Fromm, *Ibid.*, 399, 366 (1913).

$$2(CH_3)_3N{=}O = 2(CH_3)_3N + O_2.$$

$$(CH_3)_3N{=}O = (CH_3)_2N{-}H + CH_2O.$$

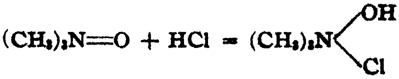
Dunstan and Goulding, in summing up the behavior of amine oxides, said, "From a careful study of amine oxides, we conclude that the oxygen is in the 'active' condition analogous to the oxygen atom in hydrogen peroxide." In connection with similar experiments, Hantzsch and Hillard[1] said, "Since, furthermore, this reaction (*viz.*, the loss of oxygen to give trimethylamine) occurs also when a solution of trimethylamine oxide is placed in contact with silver oxide; and since, in general, the properties of the base remind one of hydrogen peroxide, it seems plausible to assume that trimethyloxyammonium hydroxide may dissociate into trimethylamine and hydrogen peroxide."

$$(CH_3)_3N(OH)_2 \rightleftarrows (CH_3)_3N + H_2O_2.$$

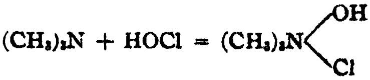
Hantzsch and Hillard suggested that the oxidation of tertiary amines by hydrogen peroxide to give hydrated amine oxides indicated that this reaction might be considered as reversible.

The Action of Hypochlorous Acid and of Bromine upon Tertiary Amines.

In this connection, some experiments of Willstätter and Iglauer,[2] and of Hantzsch and Graf[3] are significant. Willstätter studied the action of hypochlorous acid upon trimethylamine. From structural considerations alone, it would seem probable that this reaction might give the same compound which had been obtained previously by the action of hydrogen chloride upon trimethylamine oxide. *E. g.*,

(I) 

$$(CH_3)_3N{=}O + HCl = (CH_3)_3N\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix}$$

(II) 

$$(CH_3)_3N + HOCl = (CH_3)_3N\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix}$$

As a matter of fact, a totally different reaction occurred, which Willstätter expressed by the following equations:

$$(CH_3)_3N + HOCl = (CH_3)_2N{-}Cl + CH_3OH.$$

The salt (I) obtained from trimethylamine oxide *does not yield either of these products under any circumstance.*[4] Hantzsch and Graf discussed these puzzling experiments, and decided to represent the two possible compounds as "coördination isomers" in accordance with Werner's hypothesis.

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[1] Hantzsch and Hillard, *Ber.*, 31, 2058 (1898).

[2] Willstätter and Iglauer, *Ber.*, 33, 1636 (1900).

[3] Hantzsch and Graf, *Ber.*, 38, 2156 (1905).

[4] Meisenheimer, *Ber.*, 46, 1149 (1913). Trimethylamine oxide was treated with hypochlorites, but not a trace of dimethylchloroamine could be found.

$[(CH_3)_3NOH]Cl.$ From $(CH_3)_3N{=}O$ and HCl.
$[(CH_3)_3NCl]OH.$ From $(CH_3)_3N$ and HOCl.

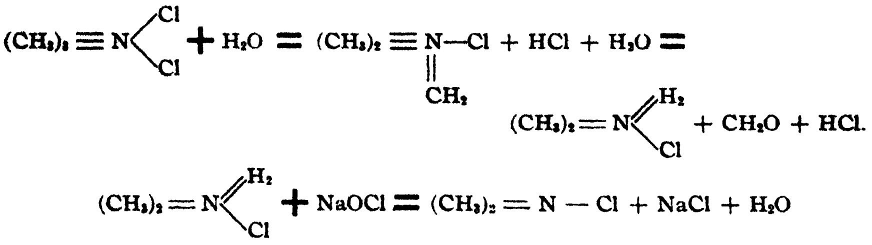
The experiments of Willstätter and Iglauer were repeated by Meisenheimer,[1] who used not only hypochlorous acid, but also hypochlorites. His experiments showed that a serious mistake had been made in the interpretation of the reaction; *formaldehyde was produced, not methyl alcohol.* In addition to dimethylchloroamine, he isolated monomethyldichloroamine, $CH_3{-}NCl_2$.

$$(CH_3)_3N + 2HOCl = (CH_3)_2N{-}Cl + CH_2O + H_2O + HCl.$$

$$(CH_3)_2N{-}{-}H + 2HOCl = (CH_3)N{=}Cl_2 + CH_2O + H_2O + HCl.$$

The reaction required a large excess of hypochlorite. When only two mol equivalents were used, the formation of the chloroamine was scarcely perceptible; the chief products in that case were unchanged tertiary amine, and a secondary amine accompanied by formaldehyde.

Meisenheimer accounted for these results by assuming that the free chlorine present in the hypochlorite reacted by addition with the tertiary amine to give $(R)_3NCl_2$, which was subsequently changed in accordance with the following equations:



$$(CH_3)_3\equiv N\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + H_2O = (CH_3)_2\equiv \underset{CH_2}{\overset{}{\underset{\|}{N}}}{-}Cl + HCl + H_2O = (CH_3)_2{=}N\begin{smallmatrix}H_2\\Cl\end{smallmatrix} + CH_2O + HCl.$$

$$(CH_3)_2{=}N\begin{smallmatrix}H_2\\Cl\end{smallmatrix} + NaOCl = (CH_3)_2 = N - Cl + NaCl + H_2O$$

In my opinion, it is quite unnecessary to assume that the dichloride is responsible for these changes, although, as will be shown later, in the case of the corresponding dibromide, it would lead to the similar reactions if it were formed. It seems entirely sufficient to assume that the hypochlorous acid reacts with the tertiary amine to give trimethylchloroammonium hydroxide, $(CH_3)_3NCl(OH)$, and that this is the substance undergoing change in these reactions. In fact, if the dichloride were formed, it would not persist to any extent as such in an alkaline medium of the character of sodium or calcium hypochlorite, but would be expected to give trimethylchloroammonium hydroxide.

The behavior of bromine towards tertiary amines led to similar anomalies. Hantzsch[2] obtained the dibromide of trimethylamine as a reddish yellow solid which melted at 85°. It had a distinct odor of bromine, and decomposed rapidly in moist air. As Hantzsch himself suggested, structural relations, pure and simple, would lead one to expect that such a dibromide might react with alkalies in much the same fashion that lead dibromide, or other similar inorganic salts, have been found to react; and that the action of alkalies upon the dibromides of tertiary amines might yield hydrated amine oxides. *E. g.*,

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[1] Meisenheimer, *Ber.*, 46, 1148 (1913).

[2] *Loc. cit.*

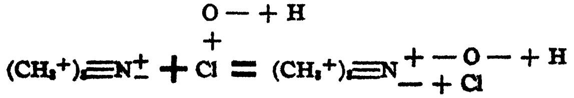
$$Pb(Br)_2 + 2KOH = Pb(OH)Br + KBr + KOH = Pb(OH)_2 + 2KBr.$$

$$(R_3)N(Br)_2 + 2KOH = (R)_3N(OH)Br + KBr + KOH = (R)_3N(OH)_2 + 2KBr.$$

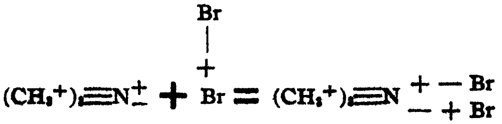
But this was not the case. Potassium hydroxide reacted with the dibromide of trimethylamine to give trimethylamine, potassium hypobromite, and potassium bromide, with small amounts of dimethylbromoamine, *but not a trace of trimethylamine oxide or its hydrate could be found.*

An Electronic Explanation of the Action of Hypochlorous Acid and of Bromine upon Tertiary Amines.

Several important conclusions may be drawn from these experiments, *viz.*, that both the bromine molecule and the hypochlorous acid molecule add to tertiary amines in such a way that the *two groups of each molecule preserve all of their distinctive electronic characteristics even after the addition has taken place.* From an electronic point of view, bromine in hypobromous acid is positive (Br^+), while it is negative (Br^-) in hydrogen bromide. The bromine molecule may be represented by the electronic formula,[1] Br+—Br. Similarly, hypochlorous acid, in accordance with its usual behavior towards organic compounds, may be written H+—O—+Cl.[2] In terms of these symbols, the addition reactions discussed above may be represented in the following manner:



$$(CH_3^+)_3{\equiv}N^{\pm}_{} + \overset{\overset{O-+H}{+}}{Cl} = (CH_3^+)_3{\equiv}N\begin{smallmatrix}+ & -O-+H\\ - & +Cl\end{smallmatrix}$$



$$(CH_3^+)_3{\equiv}N^{\pm} + \overset{\overset{Br}{|}}{\overset{+}{Br}} = (CH_3^+)_3{\equiv}N\begin{smallmatrix}+ & -Br\\ - & +Br\end{smallmatrix}$$

In at least one essential particular, the reaction of bromine upon metallic lead differs from the action of bromine upon trimethylamine, *viz.*, both bromine atoms in lead dibromide are eliminated by alkalies in the form of bromide, and must be represented as negative.[3]

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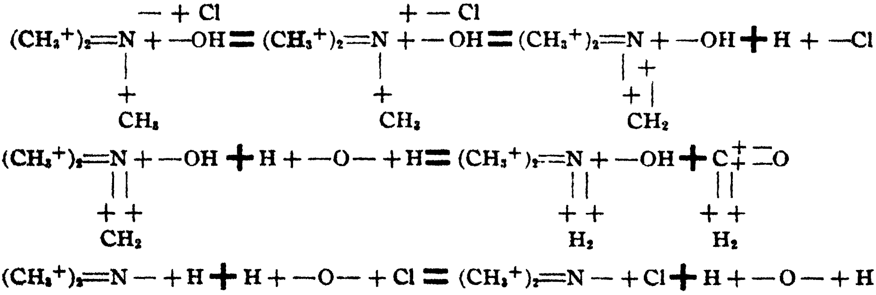
[1] The chlorine molecule was given a corresponding formula, Cl+ — Cl, by W. A. Noyes, THIS JOURNAL, 23, 463 (1901); Stieglitz, *Ibid.*, 23, 797 (1901). See Walden, *Z. physik. Chem.*, 43, 385 (1903).

[2] Stieglitz, *Loc. cit.*

[3] It is very probable that between these two extremes, there may be many cases

$$\mathrm{Pb} \mathbf{+} \mathrm{Br} + -\mathrm{Br} = \left[\mathrm{Pb}\substack{-\\+}\substack{+\\-}\substack{\mathrm{Br}\\\mathrm{Br}}\right] = \mathrm{Pb}\substack{+\\+}\substack{-\\-}\substack{\mathrm{Br}\\\mathrm{Br}}$$

The results obtained by Willstätter and Iglauer in their experiments with hypochlorous acid and tertiary amines may be interpreted electronically by assuming that the intermediate product with positive chlorine and negative hydroxyl was transformed in much the same manner as the dialkylchloroamines studied by Berg were found to change; *viz.*, through intermolecular oxidation brought about by positive chlorine. The reactions may be represented by the following equations:



$$(\mathrm{CH_3^+})_2{=}\underset{\substack{|\\+\\\mathrm{CH_3}}}{\mathrm{N}} \overset{-\,+\,\mathrm{Cl}}{+\,-\mathrm{OH}} = (\mathrm{CH_3^+})_2{=}\underset{\substack{|\\+\\\mathrm{CH_3}}}{\mathrm{N}} \overset{+\,-\,\mathrm{Cl}}{+\,-\mathrm{OH}} = (\mathrm{CH_3^+})_2{=}\underset{\substack{|\,+\\+\,|\\\mathrm{CH_2}}}{\mathrm{N}} + -\mathrm{OH} \mathbf{+} \mathrm{H} + -\mathrm{Cl}$$

$$(\mathrm{CH_3^+})_2{=}\underset{\substack{||\\++\\\mathrm{CH_2}}}{\mathrm{N}} + -\mathrm{OH} \mathbf{+} \mathrm{H} + -\mathrm{O}- + \mathrm{H} = (\mathrm{CH_3^+})_2{=}\underset{\substack{||\\++\\\mathrm{H_2}}}{\mathrm{N}} + -\mathrm{OH} \mathbf{+} \underset{\substack{||\\++\\\mathrm{H_2}}}{\mathrm{C}}\substack{+\\+}\substack{-\\-}\mathrm{O}$$

$$(\mathrm{CH_3^+})_2{=}\mathrm{N} - + \mathrm{H} \mathbf{+} \mathrm{H} + -\mathrm{O}- + \mathrm{Cl} = (\mathrm{CH_3^+})_2{=}\mathrm{N} - + \mathrm{Cl} \mathbf{+} \mathrm{H} + -\mathrm{O} - + \mathrm{H}$$

The formation of monomethyldichloroamine also is easily accounted for. Dimethylchloroamine, like the compounds of the same class studied

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in which the tautomeric equilibrium is more easily shifted by comparatively slight changes in physical or chemical conditions. Thus, phosphorus trichloride reacts with chlorine to give phosphorus pentachloride. When phosphorus pentachloride is treated with water, all of the chlorine is eliminated as hydrogen chloride. This suggests the electronic formula,

$$(\mathrm{Cl^-})_3\substack{+\\+\\+}\;\substack{+\,-\mathrm{Cl}\\+\,-\mathrm{Cl}}$$

But phosphorus pentachloride dissociates slightly at ordinary temperature, and much more completely at elevated temperature, to give phosphorus trichloride and chlorine. Assuming that the electronic formula given above represents the state of the chlorine atoms in the pentachloride, a dissociation of this kind presupposes an intramolecular oxidation, and, therefore, a condition of electronic equilibrium expressed in the following equations:

$$(\mathrm{Cl^-})_3\substack{+\\+\\+}\mathrm{P}\substack{+\,-\mathrm{Cl}\\+\,-\mathrm{Cl}} \rightleftharpoons (\mathrm{Cl^-})_3\substack{+\\+\\+}\mathrm{P}\substack{-\\+}\substack{+\\-}\substack{\mathrm{Cl}\\\mathrm{Cl}} \rightleftharpoons (\mathrm{Cl^-})_3\substack{+\\+\\+}\mathrm{P}\substack{+\\-} \mathbf{+} \mathrm{Cl} + -\mathrm{Cl}$$

Many other dissociations require similar electronic explanations. Mercuric oxide reacts with acids to give a mercuric salt and water; but when it is heated it dissociates into metallic mercury and oxygen:

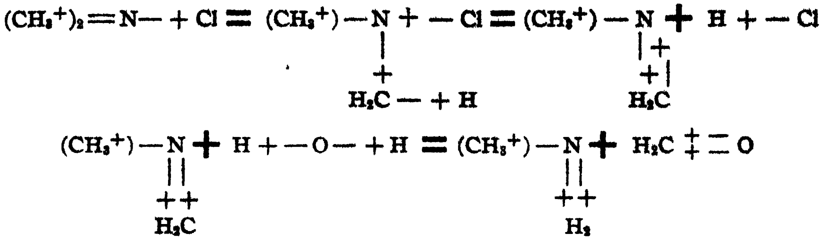
$$2\mathrm{Hg}\substack{+\\+}\substack{-\\-}\mathrm{O} \rightleftharpoons 2\mathrm{Hg}\substack{-\\+}\substack{+\\-}\mathrm{O} \rightleftharpoons 2\mathrm{Hg}\substack{-\\+} \mathbf{+} \mathrm{O}\substack{+\\-}\substack{-\\+}\mathrm{O}$$

Even water, since at high temperature it shows an appreciable dissociation into hydrogen and oxygen, must be represented thus:

$$2\mathrm{H} + -\mathrm{O}- + \mathrm{H} \rightleftharpoons 2\mathrm{H} + -\mathrm{O} + -\mathrm{H} \rightleftharpoons 2\mathrm{H} + -\mathrm{H} \mathbf{+} \mathrm{O}\substack{+\\-}\substack{-\\+}\mathrm{O}$$

These cases are merely illustrative of countless others which might be cited.

by Berg (see p. 1272) would undergo intramolecular oxidation to give a chloride, methylamine, and formaldehyde.



$$(CH_3^+)_2{=}N{-} + Cl = (CH_3^+){-}\underset{\underset{H_2C\,-\,+\,H}{+}}{\underset{|}{N}} + {-}Cl = (CH_3^+){-}\underset{\underset{H_2C}{+|}}{\underset{|+}{N}} + H + {-}Cl$$

$$(CH_3^+){-}\underset{\underset{H_2C}{++}}{\underset{||}{N}} + H + {-}O{-} + H = (CH_3^+){-}\underset{\underset{H_2}{++}}{\underset{||}{N}} + H_2C\begin{smallmatrix}+\\+\end{smallmatrix}\!=O$$

Methylamine would then be changed to methyldichloroamine by the action of the hypochlorite,

$$(CH_3^+) - N\begin{smallmatrix}-+H\\-+H\end{smallmatrix} + 2H + -O- + Cl = (CH_3^+)-N\begin{smallmatrix}-+Cl\\-+Cl\end{smallmatrix} + 2H + -OH.$$

The hydrolysis of trimethylamine dibromide by means of alkalies may be explained as follows: If complete hydrolysis occurs, the products will be trimethylammonium hydroxide, or a tertairy amine and water, a hypobromite, and a bromide.

$$(CH_3^+)_3 \equiv N\begin{smallmatrix}-&+&Br\\+&-&Br\end{smallmatrix} + 2K + -O- + H =$$

$$(CH_3^+)_3 \equiv N\begin{smallmatrix}-&+H\\+&-OH\end{smallmatrix} + K + -O- + Br + K + -Br.$$

If only partial hydrolysis takes place, the reaction may be represented by the following equation:

$$(CH_3^+)_3 \equiv N\begin{smallmatrix}-+Br\\+-Br\end{smallmatrix} + K + -O- + H = (CH_3^+)_3 \equiv N\begin{smallmatrix}-+Br\\+-OH\end{smallmatrix} + K + -Br.$$

This intermediate product should be the same as one which would be formed by the addition of hypobromous acid to trimethylamine. It would either be hydrolyzed further, or dissociate directly, into hypobromus acid and trimethylamine. On the other hand, it might undergo intramolecular oxidation, and lose formaldehyde to give dimethylamine, which would then be converted into dimethylbromoamine by the action of the hypobromite. (See reactions, (p. 1277) in the case of hypochlorous acid.) These interpretations account for all of the aberrations actually observed by Willstätter and Iglauer and by Hantzsch.

Electronic Tautomerism of Hydroxylamine and its Derivatives.

If hydroxylamine is considered from the electronic point of view, the variety of its reactions, as well as those of its derivatives, may be explained in a more satisfactory way than it has been found possible to explain them upon the basis of ordinary structural formulas. Furthermore, by simple hypotheses concerning the exchange of electrons between atoms composing these substances, the chemical changes involving oxidation and reduction, as well as molecular rearrangement, find consistent interpretations.

The spontaneous decomposition of hydroxylamine has been mentioned above. Lobry de Bruyn[1] found that samples of pure hydroxylamine, which had been kept in clean sealed glass tubes for about two years, were only partially decomposed; they all contained ammonia, nitrogen and nitrous oxide, but only two of them showed traces of nitrous acid. Lobry de Bruyn speaks of these processes as "Selbstoxidation und Reduction" in which "one part of the hydroxylamine gives oxygen and forms ammonia, while a second part suffers oxidation to hyponitrous acid and to nitrous acid which undergo further changes." Many investigators have mentioned the tremendous effect which alkalies have in accelerating this decomposition. If hydroxylamine is poured upon solid potassium hydroxide, it may even take fire and burn. Kolotow[2] studied the action of solutions of sodium hydroxide upon hydroxylammonium sulfate. The following products were formed which he expressed quantitatively in values for nitrogen based upon the fractional part of total nitrogen (16.41%) furnished by the sulfate.

		Per cent.
NH_3	=	7.12
N_2	=	6.68
N_2O	=	2.22
$NaNO_3$	=	0.39

From these experiments, and many others which might be given, it will be found that the decomposition of hydroxylamine gives chiefly ammonia and nitrogen, with some nitrous oxide, nitrous acid and nitric acid. It has also been shown that hyponitrous acid is one of the products.

If the assumption be made that the hydrogen atoms function positively in all of the following cases, the electronic equilibrium of hydroxylamine may be shown as follows:

$$\begin{tikzcd}
\text{(I)} \quad (H^+)_2 = N - + O - + H \arrow[r, shift left] \arrow[d, shift right] & (H^+)_3 \equiv N \overset{+}{-} \underset{+}{-} O \quad \text{(I}a\text{)} \arrow[l, shift left] \arrow[d, shift right] \\
\text{(II)} \quad (H^+)_2 = N + - O - + H \arrow[r, shift left] \arrow[u, shift right] & (H^+)_3 \equiv N \overset{+}{+} \overset{-}{-} O \quad \text{(IIa)} \arrow[l, shift left] \arrow[u, shift right]
\end{tikzcd}$$

A consideration of these formulas will show that (I) and (I*a*), (II) and (II*a*) represents pairs of structural tautomers, while (I) and (II), (I*a*) and (II*a*), respectively, denote pairs of electronic tautomers or electromers;[3] that is, compounds which, in the ordinary structural sense, are identical, but mutually transformable by an exchange of negative electrons between the atoms composing the molecules.

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[1] Lobry de Bruyn, *Ber.*, 27, 967 (1894).

[2] Kolotow, *J. Russ. Phys. Chem. Soc.*, 1, 295 (1893); *Ber.*, 26, 701 (1893). The figures given are those of Kolotow. With the present values of atomic weights, the percentage of nitrogen would be 17.07, instead of 16.41%.

[3] The word "electromer" was coined by H. S. Fry, and used by him in an article which appeared in the *Z. physik. Chem.*, 76, 387 (1911).

Structural tautomers (I) $\rightleftarrows$ (I*a*)
(II) $\rightleftarrows$ (II*a*)
Electronic tautomers[1] (I) $\rightleftarrows$ (II)
(I*a*) $\rightleftarrows$ (II*a*)

In terms of the electronic formulas proposed above, the spontaneous decomposition of hydroxylamine may be explained. Since the hydroxyl group in formula (I) is positive, there is no chance for this form to lose water. It is to be expected that a substance corresponding to formula (I) (or in view of the reactions of amine oxides, to formula (I*a*)), would act as an oxidizing agent, and would readily dissociate into "active oxygen" and ammonia.

$$\mathrm{(H^+)_3 \equiv N \mp \pm O = (H^+)_3 \equiv N \pm} \mathbf{+} \mathrm{\mp O.}$$

In the case of amine oxides, the oxygen either escaped as free oxygen or was used to bring about oxidation intramolecularly or intermolecularly. Similarly, hydroxylamine in alkaline solution oxidizes ferrous hydroxide to ferric hydroxide, and is converted into ammonia.

On the other hand, formula (II) would represent a substance which could lose one molecule of water, since the hydroxyl group in this case is negative,

$$\mathrm{(H^+)_2{=}N{+}{-}O{-}{+}H = H{+}{-}N\mp} \mathbf{+} \mathrm{H{+}{-}O{-}{+}H.}$$

This product of dissociation, *active imide*, corresponds in form to the univalent nitrogen derivatives which are assumed to play so important a role in the Beckmann rearrangement.[2] A substance of such a formula would be a powerful reducing agent, and would combine with the oxygen given by the dissociation of the form $\mathrm{(H^+)_3{\equiv}N{\mp}{\pm}O}$, or with oxygen furnished by other oxidizing agents, or with oxygen of the air, to give an electromer of hyponitrous acid.

$$\mathrm{H{+}{-}N\pm} \mathbf{+} \mathrm{O \pm \mp N \equiv (H^+)_3 = H{+}{-}N \mp \pm O} \mathbf{+} \mathrm{(H^+)_3 \equiv N \pm.}$$

The form, HNO, would rearrange to give hyponitrous acid, or nitrous oxide and water.

$$\mathrm{2H{+}{-}N \mp \pm O = 2H{+}{-}N\,{}^{+}_{+}\,{}^{-}_{-}\,O = (H{+}{-}O{-}{+}N\pm)_2.}$$

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[1] A third electromer, $\mathrm{(H^+)_3 \equiv N \begin{smallmatrix}-&+\\-&+\end{smallmatrix} O}$, might result from either (I*a*) or (II*a*) by an exchange of negative electrons between oxygen and nitrogen. This formula leads to no corresponding tautomer of the formula $\mathrm{H_2N{-}OH}$, since rearrangement is precluded by the fact that positive oxygen cannot hold positive hydrogen. The improbability of this formula is increased by the fact that no compounds $\mathrm{NH_5}$, $\mathrm{NR_5}$, etc., have been made. Furthermore, the compounds $\mathrm{(R^+)_3 \equiv N \begin{smallmatrix}-&+&Br\\+&-&Br\end{smallmatrix}}$ do not seem to show any tendency to become $\mathrm{(R^+)_3 \equiv N \begin{smallmatrix}-&+&Br\\-&+&Br\end{smallmatrix}}$.

[2] For the conception of univalent nitrogen as applied to the Beckmann rearrangement, see Stieglitz, *Am. Chem. J.*, 18, 751 (1896); 29, 49 (1903); Stieglitz and Earl,

Granting these statements, we are in a position to explain the fact that nitrous oxide is the chief product obtained during the action of the majority of oxidizing agents upon hydroxylamine. It may be assumed that, in the presence of an active oxidizing agent, it would not be necessary for the oxygen to be furnished by hydroxylamine itself, but that it might be taken largely, or exclusively, from the oxidizing agent, and that, especially in acid solution, this might force the hydroxylamine to react almost quantitatively through the dissociation product,[1] $H+—N\pm$, to give nitrous oxide.

If, however, no oxidizing agent, except hydroxylamine itself, is present, the chief products are ammonia and nitrogen, with small amounts of nitrous oxide, and still smaller amounts of nitrous acid and nitric acid. The formation of ammonia and nitrous oxide has been explained. To account for the nitrogen, it may be assumed that the speed of spontaneous decomposition is relatively slow, and that hyponitrous acid, formed by the oxidation of active imide, reacts with hydroxylamine to give hydroxylammonium hyponitrite, which might be expected to decompose at once to yield nitrogen and water.

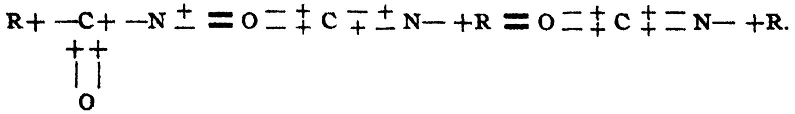
$$(NH_3(OH)ON)_2 = 2N_2 + 4H_2O.$$

In a similar manner, Wislicenus[2] found that nitrous acid reacted with hydroxylamine to give nitrous oxide and water.

Ibid., 30, 399, 412 (1903); Stieglitz and Slossen, *Ber.*, 28, 3266 (1896); 34, 1613 (1902), etc.

For an electronic interpretation in terms of univalent nitrogen see Jones, *Am. Chem. J.*, 48, 26 (1912); 50, 440 (1913); Stieglitz, THIS JOURNAL, 36, 280 (1914).

The formula, $H + — N\pm$, would act also as an oxidizing agent. It is this specific property of univalent nitrogen derivatives which has been shown to be accountable for the Beckmann rearrangement. Thus



$$R+ —\underset{\underset{O}{\|}}{\overset{}{C}}+ —N \pm = O \substack{-\\-}\substack{+\\+} C \substack{-\\+}\substack{+\\-} N— +R = O \substack{-\\-}\substack{+\\+} C \substack{+\\+}\substack{-\\-} N— +R.$$

During the rearrangement the carbon atom is oxidized by losing two negative electrons which are gained by the nitrogen atom.

[1] In acid solution, the presence of the salt, $NH_3(OH)Cl$, must be taken into consideration. Electronically, a loss of water would give a chloroamine, $H_2N + — Cl$, with negative chlorine.

$$(H^+)_3 \equiv N \substack{- + OH\\+ - Cl} = (H^+)_3 \equiv N \substack{+ - OH\\+ - Cl} = (H^+)_2 = N + —Cl + H + —OH.$$

This chloroamine might lose hydrogen chloride to give active imide $H + — N\substack{+\\-}$. It may be that this reaction is partially responsible for the changes observed in acid solution. In explaining the Beckmann rearrangement of oximes, Stieglitz has made similar assumptions concerning the intermediate products. Thus, in the case of ketoximes, Stieglitz (THIS JOURNAL, 36, 281 (1914)) assumes the intermediate product:

$$(R^+)_2 \substack{-\\-} C \substack{+\\+} \substack{-\\-} N + — Cl.$$

[2] Wislicenus, *Ber.*, 26, 77 (1893).

$$\mathrm{NH_3(OH)—ON{=}O} = \mathrm{N_2O} + \mathrm{2H_2O}.$$

If the form H+—N=O, or hyponitrous acid, continued to be oxidized, nitrous acid or even nitric acid would result.

In many respects, the reactions of hypochlorous acid resemble those of hydroxylamine, and may be explained in a very similar way by assuming positive and negative hydroxyl. It is well known that hypochlorous acid, in addition to its ability to substitute chlorine for hydrogen in organic compounds, acts as an oxidizing agent and as a reducing agent. Furthermore, on exposure to light, it dissociates into oxygen and hydrogen chloride. All of these reactions find a happy explanation if the assumption be made that hypochlorous acid behaves as a tautomeric substance in the electronic sense. Thus:

$$\underset{\text{(I)}}{\mathrm{H}+—\mathrm{O}+—\mathrm{Cl}} \rightleftarrows \underset{\text{(II)}}{\mathrm{H}+—\mathrm{O}—+\mathrm{Cl}}$$

There is also a possibility of having structural tautomers, similar to those proposed for hydroxylamine.

$$\underset{\text{(I}a\text{)}}{\mathrm{H}+—\mathrm{Cl}{}^{-}_{+}{}^{+}_{-}\mathrm{O}} \rightleftarrows \underset{\text{(II}a\text{)}}{\mathrm{H}+—\mathrm{Cl}{}^{+}_{+}{}^{-}_{-}\mathrm{O}}$$

Formula (I) explains the dissociation of hypochlorous acid in the light.

$$2\mathrm{H}+—\mathrm{O}+—\mathrm{Cl} = 2\mathrm{H}+—\mathrm{Cl} + \mathrm{O}{}^{-}_{+}{}^{+}_{-}\mathrm{O}.$$

Owing to the tautomeric equilibrium between (I) and (II), which seems to be shifted by the action of light, hypochlorous acid gradually dissociates into oxygen and hydrogen chloride. This reaction may be catalyzed in many other ways.

When hypochlorous acid acts upon organic compounds as a chlorinating agent, it does so according to formula (II), and substitutes *positive* chlorine for positive *hydrogen*. In some cases the chlorine in the organic compound retains its positive character, that is, its ability to liberate iodine from an acidulated solution of an iodide, etc. This is the case with chloroamines, chloroimidoesters, nitrogen trichloride and many other compounds. It has been shown that tetraiodomethane reacts with water to give iodoform and hypoiodous acid.[1]

$$\mathrm{I_3C}—+\mathrm{I} + \mathrm{H}+—\mathrm{O}—+\mathrm{H} = \mathrm{I_3C}—+\mathrm{H} + \mathrm{H}+—\mathrm{O}—+\mathrm{I}.$$

Bolas and Grove[2] and later Nef[3] found that tetrabromomethane, when heated with alcohol or with alcoholic potash gave bromoform, acetaldehyde and potassium bromide, but not a trace of carbonate could be found. Similarly, Nef[4] found that tetrachloromethane, with one equivalent of sodium ethylate, gave chiefly orthoformic ethyl ester, but no carbonate.

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[1] Gustavson, *Ann.*, 172, 176 (1874).

[2] *J. Chem. Soc.*, 23, 164; 24, 783; *Ann.*, 156, 60; 160, 160.

[3] Nef, *Ann.*, 308, 329 (1899).

[4] Nef, *Loc. cit.*, p. 330.

Tetraiodomethane when heated with alcohol at 100° gave a quantitative yield of iodoform. Another interesting case of a similar character was reported by Nef.[1] Chlorocyanogen and bromocyanogen, when treated with alkalies are converted into cyanates together with chlorides or bromides. But iodocyanogen under the influence of the same reagents gave a *cyanide* and an *iodate*. These reactions would suggest the following electronic formulas for these three compounds:

$$\mathrm{N}\equiv\mathrm{C}+\!-\mathrm{Cl} \qquad \mathrm{N}\equiv\mathrm{C}+\!-\mathrm{Br} \qquad \mathrm{N}\equiv\mathrm{C}-\ +\mathrm{I}$$

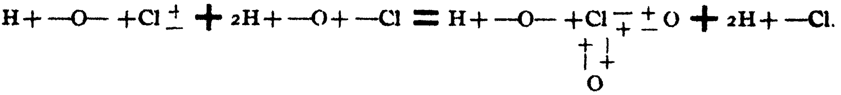
The possibility of the halogen atoms being linked to nitrogen must be taken into account, but that would not alter the conclusion concerning the positive or negative nature of the halogen atoms.

The behavior of bromophenylacetylene and iodophenylacetylene, also studied by Nef,[2] indicates that the halogen atoms in these compounds must be considered as positive, since they react with sodium ethylate or potassium hydroxide to give chiefly *phenylacetylene*, *aldehyde* (resin) and a *halogen salt*.

In other cases the characteristic properties of positive halogen are lost entirely, which implies that, after substitution has occurred, an exchange of electrons between the atom linked to halogen and positive halogen gives compounds with negative halogen.[3] This is the case with methyl chloride, chloroform, trichloracetic acid, etc.

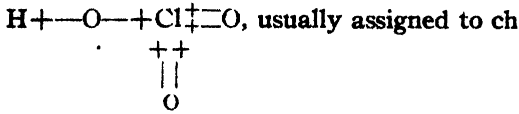
$$\mathrm{H_3C}-\!+\mathrm{H}\ \boldsymbol{+}\ \mathrm{H}+-\mathrm{O}-+\mathrm{Cl} = \mathrm{H_3C}-+\mathrm{Cl}\ \boldsymbol{+}$$
$$\mathrm{H}+\!-\mathrm{O}-\!+\mathrm{H} = \mathrm{H_3C}+\!-\mathrm{Cl}\ \boldsymbol{+}\ \mathrm{H}+\!-\mathrm{O}-+\mathrm{H}.$$

Formula (II) also explains the reducing action of hypochlorous acid which occurs when hypochlorites change to chlorates.



$$\mathrm{H}+-\mathrm{O}-+\mathrm{Cl}\overset{+}{\underset{-}{}}\ \boldsymbol{+}\ 2\mathrm{H}+-\mathrm{O}+-\mathrm{Cl} = \mathrm{H}+-\mathrm{O}-+\underset{\substack{+\,|\\|\,+\\\mathrm{O}}}{\mathrm{Cl}}\overset{-}{\underset{+}{}}\overset{+}{\underset{-}{}}\mathrm{O}\ \boldsymbol{+}\ 2\mathrm{H}+-\mathrm{Cl}.$$

By intramolecular oxidation and reduction, this electromer may pass to the form $\mathrm{H}+\!-\mathrm{O}-\!+\underset{\substack{+\,+\\|\,|\\\mathrm{O}}}{\mathrm{Cl}}\overset{+}{\underset{+}{}}\!=\!\mathrm{O}$, usually assigned to chloric acid.



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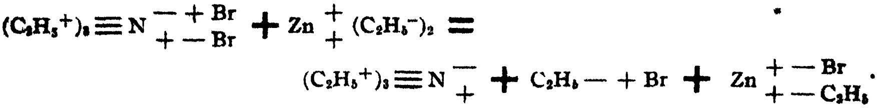
[1] Nef, *Loc. cit.*, p. 320

[2] Nef, *Loc. cit.*, pp. 292, 310, 316.

[3] Lachmann, *Am. Chem., J.* 18, 372 (1896), in an unsuccessful attempt to prepare $\mathrm{N(C_2H_5)_5}$, found that zinc diethyl reacted with triethylamine dibromide to give triethylamine, ethyl bromide, and zinc ethyl bromide. Electronically expressed:



$$(\mathrm{C_2H_5}^+)_3\equiv\mathrm{N}\begin{smallmatrix}-\,+\,\mathrm{Br}\\+\,-\,\mathrm{Br}\end{smallmatrix}\ \boldsymbol{+}\ \mathrm{Zn}\begin{smallmatrix}+\\+\end{smallmatrix}(\mathrm{C_2H_5}^-)_2 =$$
$$(\mathrm{C_2H_5}^+)_3\equiv\mathrm{N}\begin{smallmatrix}-\\+\end{smallmatrix}\ \boldsymbol{+}\ \mathrm{C_2H_5}-+\mathrm{Br}\ \boldsymbol{+}\ \mathrm{Zn}\begin{smallmatrix}+\,-\,\mathrm{Br}\\+\,-\,\mathrm{C_2H_5}\end{smallmatrix}.$$

Here again negative ethyl may be assumed to combine with positive bromine to give in the first place, $\mathrm{C_2H_5}-\dotplus\mathrm{Br}$, which passes to the usual ethylbromide, $\mathrm{C_2H_5}+-\mathrm{Br}$, that is, to the ethyl bromide which gives ethylalcohol and hydrogen bromide upon hydrolysis.

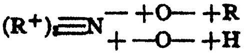
Electromers and Stereomers with Positive and Negative Hydroxyl or Alkoxyl.

It has been shown in a fairly conclusive manner that the hydroxyl group in hydroxylamine may function positively. If the hydroxyl group in hydroxylamine be regarded as positive, and if this condition of the hydroxyl group be retained in the alkyl (aryl) derivatives, two inferences concerning the behavior of substituted hydroxylamines must follow logically.

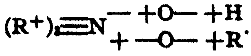
(1) Compounds containing in their formula the group $>N—OH$ or the group $>N—OR$ should show different physical and chemical properties, depending upon the nature of the hydroxyl or alkoxyl group, *i. e.*, whether it is negative (I) or positive (II).

$$\underset{\text{(I)}}{>N+—O—+R} \qquad\qquad \underset{\text{(II)}}{>N—+O—+R}$$

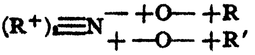
Then, again, provided one of the hydroxyl groups is positive and the other negative, compounds of the type, $(R)_3N(OH)_2$, should exist in two isomeric forms (electromers) when one of the hydrogen atoms is replaced by a single radical, R; and, furthermore, there should be two distinct isomers (electromers) if two of the hydrogen atoms are replaced simultaneously by dissimilar radicals, R and R′.



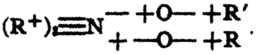
$$(R^+)_3\equiv N\begin{array}{l} -\;+O-\;+R \\ +\;-O-\;+H \end{array}$$



$$(R^+)_3\equiv N\begin{array}{l} -\;+O-\;+H \\ +\;-O-\;+R \end{array}$$



$$(R^+)_3\equiv N\begin{array}{l} -\;+O-\;+R \\ +\;-O-\;+R' \end{array}$$



$$(R^+)_3\equiv N\begin{array}{l} -\;+O-\;+R' \\ +\;-O-\;+R \end{array}$$

(2) Compounds of the formula, $R,R',R'',N(OH)_2$, in which there are three different alkyl (aryl) radicals linked to the nitrogen atom should exist in *stereoisomeric modifications*, provided one hydroxyl group is *negative* and the other one is *positive*. By the action of an optically active acid, *e. g.*, *d*-bromocamphorsulfonic acid or *d*-tartaric acid, a racemic compound obtained by synthesis should be resolved into a dextro- and a levo-modification. Optical activity might even persist in the corresponding amine oxides, $R,R',R'',N\overset{\pm}{\mp}O$. Although the two hydroxyl groups are *structurally alike*, they are totally different *electronically*. Consequently, the nitrogen atom is linked to "*five different radicals*," and, in this respect, compounds of these types may be compared to substituted ammonium compounds of the type $R,R',R'', R''', N—X$, which have been repeatedly resolved into optically active forms.[1]

It is a remarkable fact that experimental evidence supporting both of these deductions has been presented quite recently, and a brief survey of the facts may be taken up here.

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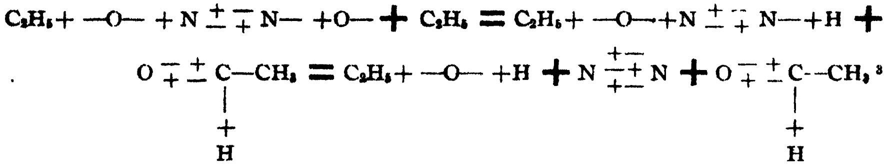
[1] LeBel, *Compt. rend.*, 112, 724 (1891); 129, 548 (1899); *Ber.*, 33, 1003 (1900); Wedekind, *Ber.*, 32, 517, 3561 (1899); 35, 766 (1902); 36, 3791 (1903); 38, 1838 (1905); Wedekind and Oberheide, *Ibid.*, 37, 2712, 3894 (1904); Wedekind and Froelich, *Ibid.*, 38, 3438 (1905); Pope and Peachey, *J. Chem. Soc.*, 75, 1127 (1899); Pope and Harvey, *Ibid.*, 79, 828 (1901).

1. Electromers.—In the first place, the chemical behavior of "diazoethoxane," studied by Zorn[1] many years ago, may be described. Zorn noted, with some surprise, that hydrolysis of this compound, structurally an ester of hyponitrous acid, did not give hyponitrous acid. This fact even caused him to write the formula with a question mark after it.[2] When an attempt was made to hydrolyze this compound by heating it with water, the products were *ethyl alcohol, acetaldehyde,* and *nitrogen.*

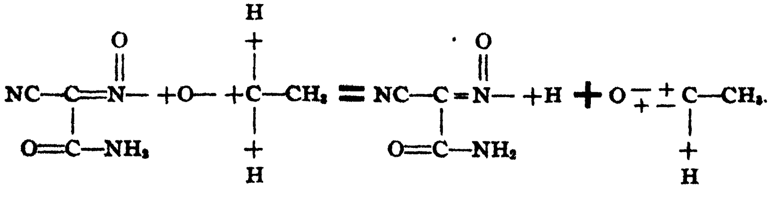
$$C_2H_5—O—N{=}N—O—C_2H_5 = C_2H_5—OH + N_2 + CH_3CHO.$$

This singular reaction finds a plausible interpretation, if the assumption be made that the two ethoxy groups are different electronically; *i. e.,* one of them negative and one of them positive. The following equations would then portray the reaction:



$$C_2H_5+ —O— +N \pm \mp N— +O— + C_2H_5 = C_2H_5+ —O— +N \pm \mp N— +H + O \mp \pm \underset{\substack{|\\+\\H}}{C}—CH_3 = C_2H_5+ —O— +H + N \overset{+-}{\underset{+-}{\mp\pm}} N + O \mp \pm \underset{\substack{|\\+\\H}}{C}—CH_3,^{3}$$

There are many other instances of a similar kind in which esters of oximes or isonitro compounds have changed to aldehydes and oximido compounds. Thus, when Nef[4] heated the ethyl ester of fulminuric acid with water, he found that it gave desoxyfulminuric acid (cyanisonitrosoacetamide) and acetaldehyde. Here, again, it is highly probable that the ethoxy group should be represented as positive ($+O—+C_2H_5$), and that the reaction proceeded as follows:



$$NC—\underset{\substack{|\\O{=}C—NH_2}}{C}{=}\overset{\substack{O\\\|}}{N}— +O— +\overset{\substack{H\\+\\|}}{\underset{\substack{|\\+\\H}}{C}}—CH_3 = NC—\underset{\substack{|\\O{=}C—NH_2}}{C}{=}\overset{\substack{\cdot\ O\\\|}}{N}— +H + O \mp \pm \underset{\substack{|\\+\\H}}{C}—CH_3.$$

This nitroso compound would rearrange to give the isonitroso compound, and the aldehyde, an electromer of acetaldehyde, would become $O \mp \pm CH(CH_3)$. Another instance of a similar character was described by

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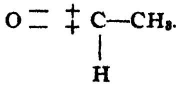
[1] Zorn, *Ber.*, 11, 1630 (1878); 15, 1008 (1882).

[2] Meyer and Jacobson, "Lehrbuch," I, p. 308.

[3] This formula represents an electromer of acetaldehyde

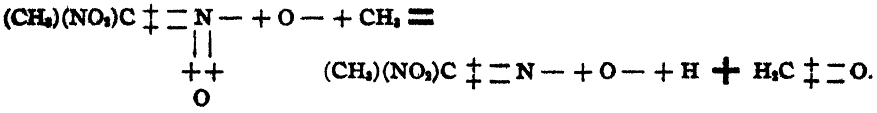


$$O \mp \pm \underset{\substack{|\\H}}{C}—CH_3.$$

The same may be true of the formula assigned to nitrogen with respect to nitrogen.

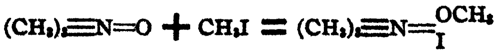
[4] Nef, *Ann.*, 280, 328 (1894); Schultz, *Ber.*, 42, 738 (1909).

Nef.[1] The silver salt of dinitroethane reacted with methyl iodide to give formaldehyde and ethylnitrolic acid. It may be assumed that the intermediate ester with positive methoxyl, $+O—+CH_3$, was unstable and dissociated at once.

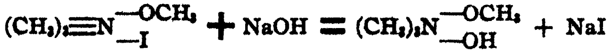


$$(CH_3)(NO_2)C \ddagger \overset{-}{-} \underset{\underset{O}{++}}{N} - +O - +CH_3 = (CH_3)(NO_2)C \ddagger \overset{-}{-} N - +O - +H + H_2C \ddagger \overset{-}{-} O.$$

Certain experiments described by Meisenheimer[2] are still more interesting. In an article[3] concerning the "Non-equivalence of the Five Valences of Nitrogen," Meisenheimer describes the preparation of two isomeric compounds of the type $(R)_3\equiv N(OCH_3)(OH)$. The *first* isomer was prepared by the action of methyl iodide upon trimethylamine oxide, and the subsequent replacement of iodine by hydroxyl. Thus:

1. 

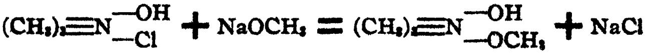
$$(CH_3)_3\equiv N=O + CH_3I = (CH_3)_3\equiv N=\genfrac{}{}{0pt}{}{OCH_3}{I}$$

2. 

$$(CH_3)_3\equiv N\genfrac{}{}{0pt}{}{-OCH_3}{-I} + NaOH = (CH_3)_3N\genfrac{}{}{0pt}{}{-OCH_3}{-OH} + NaI$$

(A)

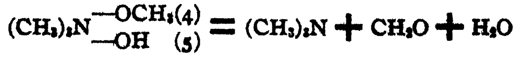
The *second* isomer was secured by the action of sodium methylate upon the salt obtained by treating trimethylamine oxide with hydrogen chloride.



$$(CH_3)_3\equiv N\genfrac{}{}{0pt}{}{-OH}{-Cl} + NaOCH_3 = (CH_3)_3\equiv N\genfrac{}{}{0pt}{}{-OH}{-OCH_3} + NaCl$$

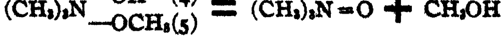
(B)

The two forms, (A) and (B), are identical *except for the order in which the hydroxyl group and the methoxyl groups were introduced.* In (B), as Meisenheimer said, the methoxyl group is linked to the "*fifth* valence," or the one which usually engages the *acid radical;* while it is linked to the "*fourth* valence" in formula (A). But these two substances are fundamentally different. This is easily demonstrated by a study of their solutions. When a water solution of trimethylmethoxyammonium hydroxide (A) was heated, it decomposed quantitatively in accordance with the following equations:

(A) 

$$(CH_3)_3N\genfrac{}{}{0pt}{}{-OCH_3(4)}{-OH\ \ (5)} = (CH_3)_3N + CH_2O + H_2O$$

While trimethylhydroxyammonium methylate (B) showed a totally different behavior.

(B) 

$$(CH_3)_3N\genfrac{}{}{0pt}{}{-OH\ \ (4)}{-OCH_3(5)} = (CH_3)_3N=O + CH_3OH$$

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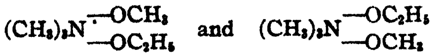
[1] Nef, *Loc. cit.*, p. 282.

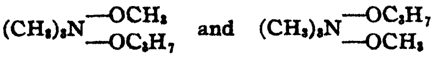
[2] Meisenheimer, *Ann.*, 385, 117 (1911); 396, 75 (1912); 397, 213 (1912); 399, 371 (1913).

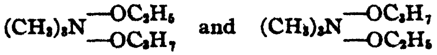
[3] Meisenheimer, *Ann.*, 397, 273 (1913).

In addition to these compounds, Meisenheimer prepared a number of isomeric mixed dialkyl compounds.

E. g.,

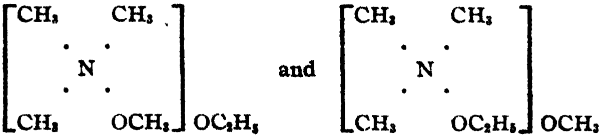
1\.

$(CH_3)_3N\genfrac{}{}{0pt}{}{-OCH_3}{-OC_2H_5}$ and $(CH_3)_3N\genfrac{}{}{0pt}{}{-OC_2H_5}{-OCH_3}$

2\.

$(CH_3)_3N\genfrac{}{}{0pt}{}{-OCH_3}{-OC_3H_7}$ and $(CH_3)_3N\genfrac{}{}{0pt}{}{-OC_3H_7}{-OCH_3}$

3\.

$(CH_3)_3N\genfrac{}{}{0pt}{}{-OC_2H_5}{-OC_3H_7}$ and $(CH_3)_3N\genfrac{}{}{0pt}{}{-OC_3H_7}{-OC_2H_5}$

In every case, water decomposed each of these six compounds to give a tertiary amine, an alcohol, and an aldehyde; but, invariably, the radical which was eliminated as aldehyde was the radical which occupied "position four (4)"and the group eliminated as alcohol always occupied "position five (5)." Meisenheimer stated that he never obtained even recognizable traces of the aldehyde, which should have resulted if the group attached in position five had separated in that form. His conclusions may be stated in his own words: "Durch diese Reaktion ist bewiesen, dass die beiden Alkoxygruppen nicht in gleicher Weise an das Stickstoffatom gebunden sind."

Meisenheimer considered various possible explanations, such as the oxonium formula, Werner's ammonium formula, and the oxonium formula of Werner. The discussion of these points cannot be taken up here, but may be found by reference to the original articles. After presenting evidence for and against various views, Meisenheimer finally decided to formulate his compounds in the symbolism of Werner's ammonium theory. Thus:


$$\left[\begin{array}{ccc} CH_3 & & CH_3 \\ & \cdot\ \cdot & \\ & N & \\ & \cdot\ \cdot & \\ CH_3 & & OCH_3 \end{array}\right] OC_2H_5 \quad \text{and} \quad \left[\begin{array}{ccc} CH_3 & & CH_3 \\ & \cdot\ \cdot & \\ & N & \\ & \cdot\ \cdot & \\ CH_3 & & OC_2H_5 \end{array}\right] OCH_3$$

However, he was not entirely satisfied with Werner's symbols, and said, "Dass die obigen Formeln nur dann richtig sind wenn mann sie anders interpretiert als A. Werner es tut." Meisenheimer, in contrast to Werner, assumed that all five radicals are bound by "haupt" valences to nitrogen, four in the inner zone and one in the outer zone. But he considered that the ammonium compounds differed from such compounds as $(CrCl_2(OH_2)_4)$-Cl, etc., in that all four coördination positions of nitrogen are occupied by radicals with "haupt" valences, and that the one in the outer zone is also linked by a "haupt" valence, but it does not have so firm a linking.

The key to these disputed relations is easily furnished, in terms of the electronic conception, by assuming that the one hydroxyl (or alkoxyl group) is positive and the other negative; or, translated into Meisenheimer's[1] language, the "fourth valence" of nitrogen is linked to a positive hydroxyl or alkoxyl group, while the "fifth valence," or the one which usually engages the acid radical, is linked to a negative hydroxyl or alkoxyl group. Thus:

$$\text{(A)}\quad (CH_3^+)_3\equiv N^{-}_{+}\begin{matrix} +O- & +CH_3 & (4)\\ +-O- & +H & (5)\end{matrix} = (CH_3^+)_3\equiv N^{-}_{+}\begin{matrix} +H & \\ +-O- & +H\end{matrix} + H_2C^{-}_{+}{}^{\pm}O$$

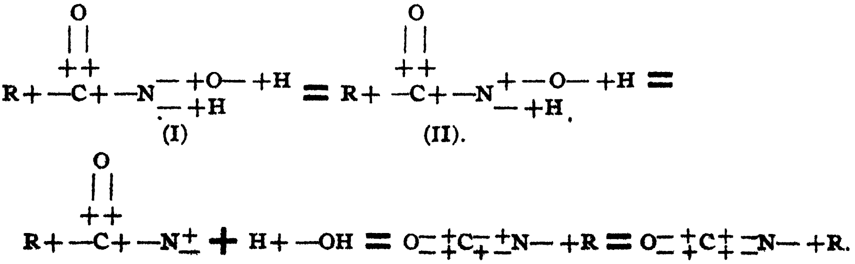
$$\text{(B)}\quad (CH_3^+)_3\equiv N^{-}_{+}\begin{matrix} +O- & +H & (4)\\ +-O- & +CH_3 & (5)\end{matrix} = (CH_3^+)_3\equiv N^{-}_{+}{}^{\pm}O + CH_3+-O-+H$$

To illustrate the decomposition of the di-derivatives, one set of equations may be given.

$$(CH_3^+)_3\equiv N^{-}_{+}\begin{matrix} +O- & +CH_3(4)\\ +-O- & +C_2H_5(5)\end{matrix} = (CH_3^+)_3\equiv N^{\pm} + C_2H_5+\ -O-\ +H + \overset{H_2}{C}{}^{-}_{+}{}^{\pm}O$$

$$(CH_3^+)_3\equiv N^{-}_{+}\begin{matrix} +O- & +C_2H_5(4)\\ +-O- & +CH_3(5)\end{matrix} = (CH_3^+)_3\equiv N^{\pm} + CH_3+-O-+H + CH_3\overset{\overset{H}{|}}{C}{}^{-}_{+}{}^{\pm}O$$

These facts make it highly probable that the hydroxyl group in hydroxylamine, and in its derivatives generally, may function positively. This applies to aldoximes, ketoximes, hydroxamic and hydroximic acids, isonitro compounds and many others which might be mentioned. The probability of tautomerism in the electronic sense, which would give compounds with negative hydroxyl, must be postulated for all such compounds. To illustrate this relation, the case of compounds undergoing Beckmann rearrangement[2] may be given.



$$R+-\overset{\overset{O}{\|}}{\overset{++}{C}}+-N^{-}_{-}\begin{matrix} +O- & +H\\ +H & \end{matrix} = R+-\overset{\overset{O}{\|}}{\overset{++}{C}}+-N^{+}_{-}\begin{matrix} +-O- & +H\\ +H & \end{matrix} =$$

(I) (II).

$$R+-\overset{\overset{O}{\|}}{\overset{++}{C}}+-N^{\pm} + H+-OH = O^{-}_{-}{}^{+}_{+}C^{-}_{+}{}^{\pm}N-+R = O^{-}_{-}{}^{+}_{+}C^{+}_{+}{}^{-}_{-}N-+R.$$

Formula (I) must pass to Formula (II) before a molecule of water can be lost to give univalent nitrogen; this is accomplished by an exchange of negative electrons between the nitrogen atom and the oxygen atom; that is, formula (I) is a tautomeric electromer of Formula (II).

2. *Stereomers.*—Meisenheimer[3] was the first to observe that amine oxides with three different radicals, R, R′, R″, N=O, could be resolved into enantiomorphous modifications. Amine oxides of this kind were prepared by oxidizing tertiary amines with hydrogen peroxide or Caro's

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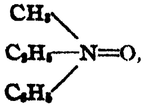
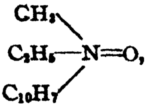
[1] Meisenheimer, *Ann.*, 399, 372 (1913).

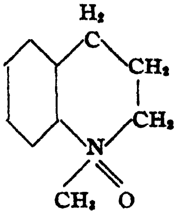
[2] Jones, *Am. Chem. J.*, 48, 1 (1912); 50, 414 (1913); Stieglitz, THIS JOURNAL, 36, 288 (1914) note.

[3] Meisenheimer, *Ber.*, 41, 3973 (1908); *Ann.*, 385, 117 (1911).

acid. Meisenheimer and his co-workers prepared methylethylaniline oxide, methylethyl-β-naphthylamine oxide and kairoline oxide



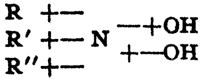




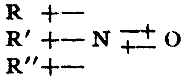
The racemates were resolved by means of *d*-bromocamphorsulfonic acid or *d*-tartaric acid. After fractional crystallization and separation, each salt was converted into the active picrate, which was changed to the corresponding active chloride, and finally, into the active amine oxide itself.

Previous attempts to resolve compounds with two like radicals, Na_2bcd, have been fruitless.[1] Even compounds more closely allied to these amine oxides in form, such as *N*-methylpicolinium salts, *N*-methylquinolinium salts, could not be resolved by H. O. Jones.[2] Meisenheimer takes it for granted that an explanation of the stereoisomerism is provided when he has called attention to the fact that, in the amine oxides, the doubly bound oxygen engages the valence which usually holds the acid radical, while in the case of the compounds studied by H. O. Jones, only non-ionizable valences have been displaced by doubly bound carbon.

It seems that a more consistent explanation may be offered in terms of the electronic view point. If the amine oxides and their hydrates have the following formulas:



$$\begin{matrix} \text{R}\ +- & & \\ \text{R}'\ +- & \text{N} & \begin{matrix} -+\text{OH} \\ +-\text{OH} \end{matrix} \\ \text{R}''+- & & \end{matrix}$$



$$\begin{matrix} \text{R}\ +- & & \\ \text{R}'\ +- & \text{N} \mathrel{\substack{-+\\ +-}} \text{O} \\ \text{R}''+- & \end{matrix}$$

the nitrogen atom in either event *does not hold two like groups* since the properties of positive and negative hydroxyl are as divergent as those of positive and negative chlorine. In this respect, the conditions are not the same as those in ammonium compounds of the form, Na_2bcd.

It must be assumed that the linking —N$\mathrel{\substack{-+\\ +-}}$O is similar to the grouping —N$\begin{smallmatrix}-+\text{OH}\\ +-\text{OH}\end{smallmatrix}$ in so far as its effect upon the asymmetry[3] of the molecule is concerned. The question may be raised, "Why should compounds of the type RR′R″N=O show optical activity while compounds of the type RR′R″N=C< do not?" In a previous article[4] it was shown that systems containing the carbon nitrogen linking, C=N, tend to assume a condition in which the carbon atom is as fully oxidized as possible and the nitrogen atom as fully reduced, *viz.*, $>C\overset{+\;-}{\underset{+\;-}{=}}N-$. Therefore, in the cyclic compounds studied by H. O. Jones, we should have

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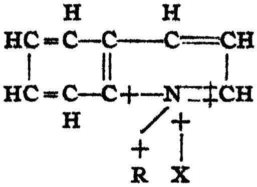
[1] Aschan, *Z. physik. Chem.*, 46, 293 (1903); Scholtz, *Ber.*, 43, 2121 (1911).

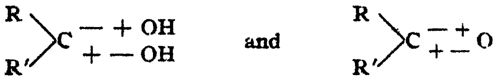
[2] H. O. Jones, *J. Chem. Soc.*, 83, 1400 (1903).

[3] The amine oxides dissolved in benzene often show very large rotations.

[4] Jones, *Am. Chem. J.*, 50, 440 (1913).



In other words, the nitrogen atom is linked to only four different groups, since the linking $\equiv N\overset{-\;+}{\underset{-\;+}{=}}C<$, is synonymous with Na_2bcd. It does not seem improbable, however, that some day conditions may be found to stabilize the system $\equiv N\overset{-\;+}{\underset{+\;-}{=}}C<$ in certain compounds, which may be expected to show optical activity. Furthermore, it may be predicted that compounds of the form



$$\begin{matrix}R\\R'\end{matrix}\!>C\begin{matrix}-+OH\\+-OH\end{matrix} \quad \text{and} \quad \begin{matrix}R\\R'\end{matrix}\!>C\overset{-\;+}{\underset{+\;-}{=}}O$$

will be found to show activity if they are ever prepared. Many other possibilities of a similar character suggest themselves.

When the existence of isomers among organic compounds was first recognized, Faraday[1] said, "In reference to the existence of bodies composed of the same elements, and in the same proportion, but differing in their qualities, it may be observed, that, now we are taught to look for them, they will probably multiply on us." In the opinion of the author, we are in much the same position at the present time with respect to these new isomers which depend upon the distribution of electrons and their exchange; and it is not improbable that they will "multiply on us" in the future.

CINCINNATI, O.

[COMMUNICATION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN.]

FORMS OF SULFUR IN PLANT MATERIALS AND THEIR VARIATION WITH THE SOIL SUPPLY.[2]

BY W. H. PETERSON.

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Sulfur occurs in plant and animal tissues chiefly in the form of proteins, volatile compounds, as the mustard oils, and sulfates. In the proteins, it is known to exist as the amino acid, cystine, but in spite of much investigation, no other sulfur bearing compound has been isolated from the products of protein hydrolysis. Much evidence, however, has been gathered to indicate the existence of sulfur in other forms than cystine in the protein molecule. Johnson,[1] reviewing the literature on this subject, was led to believe that other sulfur linkages than that illustrated by cystine may occur in these substances. Arguing from a theoretical point of view, he pointed out the close analogy existing between oxygen and sulfur groupings, and the possibility of sulfur functioning in much the same way as oxygen in tying together the protein molecule. He has prepared many synthetic compounds showing this similarity, but, as yet, has not shown the existence of any new sulfur linkage in the protein itself.

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[1] Faraday, *Phil. Trans.*, 440, (1825).

[2] This paper represents a thesis submitted to the Graduate Faculty of the University of Wisconsin in partial fulfillment for the degree of doctor of philosophy. Published with the permission of the Director of the Agricultural Experiment Station.

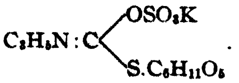
That sulfur does function in other protein linkages than the mercapto of cystine has been shown by Barger and Ewin,[2] who isolated a betaine closely related to histidine, in which the sulfur group (—CSNH) was found.

The recent work of Levene[3] in isolating a sulfatide from the brain, though not related to sulfur in the protein molecule, is closely associated with the larger subject of sulfur in plant and animal material.

Compounds Yielding Volatile Sulfur-Glucosides.—Besides sulfur in proteins, many plants contain volatile forms of sulfur, as is best illustrated by the mustard oil, allyl-*iso*-thiocyanate, the chief volatile compound existing in black mustard. Allyl sulfide, vinyl sulfide, mercaptan, and other volatile complex organic sulfides, have been obtained from onions and garlic. These volatile bodies are most abundant in the Cruciferae, but are contained also in many members of the Resedaceae, Capparidaceae, Tropaeolaceae, Liliaceae and other families.

The mustard oils do not occur as such in the plant, but as glucosides, the best known of which are sinigrin, found in black mustard, and sinalbin in white mustard.

That sinigrin contained sulfur was known to Fourcray and Tingry,[4] Henry and Garot,[5] Pelouze and Dumas,[6] Loewig[7] and others. Will and Körner[8] were the first to determine its composition and described a method for its preparation. Later, Gadamer[9] worked out its true composition and suggested as its formula



$$C_3H_5N{:}C\begin{cases}OSO_3K\\ S.C_6H_{11}O_5\end{cases}.$$

A sinigrin splitting enzyme, discovered by Ban Bussy,[10] which he named myrosin, decomposes the glucoside into allyl-*iso*-thiocyanate, glucose and acid potassium sulfate, according to the following equation:

$$C_{10}H_{16}NS_2KO_9 + H_2O = C_3H_5NCS + C_6H_{12}O_6 + KHSO_4$$

A very extensive study of myrosin was made by Grignard[11] with reference to its distribution, preparation, properties and activity. Sinalbin and other sulfur-containing glucosides are much more complex, and less is known of them than of sinigrin. In many cases the quantity of glucoside present is small and its separation from other organic matter is very difficult.

The methods used for the determination of volatile sulfur all begin with grinding the material, whereby the enzyme, coming in contact with the glucoside, sets free the volatile mustard oil. This is then distilled out, with or without the aid of steam, and the sulfur in the distillate determined by various methods. The earliest method, that of Dietrich,[12] was to collect the distillate in a 10% ammonia solution, when the allyl-*iso*-thiocyanate combines with the ammonia to form allyl-thiourea, $C_3H_5NH.(NH_2)CS$. On adding silver nitrate to this solution, silver sulfide is precipitated; this is then filtered off and the sulfur therein calculated to the corresponding allyl-*iso*-thiocyanate.

Firbas[13] modified this method by using standard silver nitrate and, by titrating the excess of silver nitrate, obtained a check on his results. Vuillemin[14] obtained better results by adding alcohol to the ammonia, while Jorgensen[15] evaporated the solution of allyl-thiourea to dryness and then weighed and checked his results by determining the content of nitrogen in the dried residue.

An oxidation method was devised by Shiet,[16] who collected the distillate in alkaline permanganate, and, after removing the excess of permanganate with alcohol, precipitated the sulfates present with barium chloride.

Mann[17] extracted the mustard oil from the distillate by means of rhigolene, evaporated off the rhigolene in an ingenious apparatus and weighed the mustard oil directly.

The most widely used of these methods is that of Dietrich, with its several modifications. This is the method that was first employed in the experimental part of this paper; it was, however, abandoned, primarily because not all the volatile sulfur could be driven out by distillation. A blackening of the distillate appeared on the addition of silver nitrate long after a precipitate ceased to come down. The volume of the distillate made it exceedingly difficult to handle, so the oxidation in a combustion furnace, described later, was finally adopted.

Sulfates.—Arendt, Ulricht, E. Schulze, Berthelot and Andre, Fraps,[18] and recently Thompson,[19] have investigated the amount of sulfates in plants and found it to vary within wide limits, according to the amount in the soil, the parts of the plant, and the stage of growth.

Relation of Sulfur to Agriculture.—The determination of volatile sulfur has been limited almost entirely to mustard and rape seed. A pretty thorough review of the literature shows no data concerning the amount of volatile sulfur in the common farm crops such as rutabagas, turnips, sugar beets, cabbage, onions, etc. The question as to the amount of this volatile sulfur, the amount of sulfur in the form of sulfates, and other possible forms of sulfur in the plant, has arisen as a result of the work done three years ago at this station on the amount of sulfur contained in farm crops and the supply of sulfur in the soil. In this paper, Hart and Peterson[20] showed that much larger amounts of sulfur were contained in plant material than had hitherto been suspected, and that the supply of this element in the soil was lower on the average than that of phosphorus, the necessity for conservation and maintenance of which in the soil has been generally recognized for many years.

Shedd,[21] in the analyses of forty Kentucky soils, has shown a loss of sulfur in practically every comparison of the cultivated soil with the virgin soil. This loss amounted to from 3–42% in the surface soils, and from 5–56% in the subsoils, and occurred in many instances even though the soils had been fertilized.

French investigators[22] have, for a long time, been experimenting with elemental sulfur and carbon disulfide in relation to increased crop production. The cause of increased yields has generally been attributed to an antiseptic action of the sulfur in the soil, whereby certain organisms unfavorable to the growth of the plant have been suppressed and the desirable ones permitted to develop. More recently the role of sulfur as a fertilizer has been considered by them.

The utilization, forms, and distribution of sulfur in plants, are questions which have arisen as a result of the increased importance of sulfur in relation to crops and soils, and the adjoined data have been gathered in an attempt to get more light on these questions.

Experimental Part.

It was planned to dissect the sulfur of the plant into four parts: volatile sulfur, sulfates, total soluble sulfur, and insoluble sulfur. The third of these includes the second, and by subtracting the sulfates from the total soluble sulfur, we have what is there probably in the form of soluble proteins. This, together with the insoluble sulfur, represents probably the total sulfur of the proteins.

Determination of Volatile Sulfur.—To get at the volatile sulfur in rutabagas, Dietrich's modified method was used at first, but because of the difficulties already mentioned, it was abandoned. Collecting the volatile sulfur in alkaline permanganate gave lower results than Dietrich's method, and the same objection, *i. e.*, a very large volume of distillate to deal with, operated here. For example, with 200 g. of green rutabagas, 2000 cc. of distillate did not seem to remove all the sulfur, since a blackening of the last 200 cc. ensued on the addition of silver nitrate. For this reason it was impossible to tell when to stop, and the discordant weights of silver sulfide obtained bore out the ocular evidence.

During these preliminary experiments, it was noticed that total sulfur, determined on the green rutabagas and on the same sample after drying in the steam oven at 95°, gave uniformly lower results, indicating the loss of volatile sulfur on drying. This suggested the idea of drying the material in a closed receptacle and determining the sulfur in the evolved vapors. After numerous attempts, the following method was worked out and used subsequently in all analyses.

Two hundred grams of material were placed in a one-inch tube 25 inches long, having a right-angle bend at each end with 4 to 5 inches of upright—in other words, a long U tube. This was immersed in a trough containing a strong brine of calcium chloride, and the tube connected to the hard glass tube in a combustion furnace. This combustion tube was filled with copper oxide filings. To the combustion tube was connected a wash bottle, half filled with glass beads and strong potassium hydroxide solution, and immersed in a bath of cold water. The wash bottle was connected to the suction pump, so that air could be drawn through the whole system. To the other end of the drying tube was attached a wash bottle filled with strong sulfuric acid, and, preceding this, another wash bottle half filled with glass beads and potassium hydroxide. The air entering the apparatus then passed first through the potassium hydroxide, whereby any hydrogen sulfide and sulfur dioxide were removed. Then it was dried in the sulfuric acid bottle, passed through the drying tube, combustion tube, and absorption bottle successively. All stoppers used were of cork and, where rubber connections had to be employed, the ends of the glass tubes were placed in contact with one another so as to expose as little of the rubber tubing as possible to the gases. The rubber connection between the combustion tube and the absorption bottle was wrapped with a cloth and kept wet during the entire period. The whole system was tested for leaks before beginning the drying, by closing the entering tube with a pinchcock and then turning on full suction. A vacuum was thus created and any leaks disclosed. These were sealed with gelatine until no gas bubbles passed through the absorption bottle at the end of the apparatus. Heat was then applied to the calcium chloride bath, air admitted slowly to the apparatus, and the drying continued until the material in the drying tube appeared dry. This required from six to nine hours, and during this time a constant level of water was maintained in the bath and the temperature not allowed to rise above 95–100°.

After drying the material, the apparatus was cooled, disconnected, and the copper oxide filings removed from the combustion tube. Almost invariably several blue crystals of copper sulfate could be detected among the filings. These were boiled to dissolve out the copper sulfate, filtered and the sulfate precipitated with barium chloride.

The solution in the absorption bottle, now much increased by the condensed water from the green material, was washed out, combined with the washings from the copper oxide, concentrated on the water bath, filtered, cooled, and carefully neutralized in the cold with hydrochloric acid. This neutral solution was then poured slowly into bromine water, heated to oxidize any sulfites, and the resulting sulfates precipitated with barium chloride.

In the earlier determinations, the copper oxide washings and the absorption solution were combined and the sulfates determined in this solution, but in the later determinations the two were kept separate and the barium sulfate precipitated in each. It was found that most of the sulfur was fixed by the copper oxide and only where the total barium sulfate amounted to more than 50 mg. was there any sulfur in the absorption bottle.

Determination of Sulfates.—To determine the sulfates in the plant tissues, the dried material was removed from the drying tube and extracted with successive portions of water on a steam bath for 6–8 hours and the extract filtered into a volumetric flask. With 200 g. of green material, the extraction was continued until 2000 cc. had been obtained. An aliquot of this was then slightly acidified with hydrochloric acid and allowed to stand on the water bath for 24 hours to premit the precipitation of proteins and other organic materials. These were filtered off and a clear, brownish colored solution was obtained. This was heated to boiling, a slight excess of barium chloride added, and the beaker allowed to stand on the water bath over night. The precipitate thus obtained was generally somewhat discolored, but on ignition usually became white or grayish white. If it seemed to be contaminated, it was fused with sodium carbonate and reprecipitated.

Determination of Total Soluble Sulfur; Sulfates and Soluble Protein Sulfur.—Another aliquot, 250 or 500 cc., was placed in a volumetric flask, attached to a reflux condenser after adding bromine water and nitric acid, and kept warm for 10–12 hours. It was then boiled to remove the excess of bromine water and evaporated to dryness on a water bath. If very black, it was again taken up with water, more nitric acid added, and again evaporated. The residue, now slightly yellow to brown in color was dissolved in water, transferred to a nickel crucible, and evaporated; sodium peroxide was added, and the material fused over an alcohol burner. It was found quite impossible to get oxidation with nitric acid and bromine alone. Other wet oxidizing agents, such as strong hydrochloric acid and potassium chlorate or as alkaline permanganate, were tried without success. After three days' treatment with hydrochloric acid and small portions of potassium chlorate in a hot water bath, the solution still turned dark on standing, showing incomplete oxidation.

The Wolf-Osterberg[23] method for determining sulfur in organic material was tried many times and gave uniformly lower results than were obtained with the peroxide treatment. Poor duplicates were also obtained by this method.

The determination of this soluble unoxidized sulfur gave a good deal of trouble, as here most of the sulfur was lost in the preliminary experiments. Only from 60–80% of the total sulfur could be accounted for, and it was only after the method described above was employed that the sum of the parts approached the total. While the procedure outlined is somewhat long and cumbersome, it is the only one that gave satisfactory results.

Insoluble Sulfur.—The extracted residue contained some insoluble organic sulfur, which was always determined by the sodium peroxide method. If to this is added the soluble unoxidized sulfur, *i. e.*, the total soluble sulfur minus the sulfate sulfur, we have what is probably the sulfur of the protein. In Table II, giving the distribution of sulfur, this value is entered in the last column.

The methods, as outlined above, were used in the analysis of different plant materials and the data thus obtained follow:

TABLE I.—VARIOUS FORMS OF SULFUR IN PLANT MATERIAL; CALCULATED AS PER CENT. SULFUR ON MOISTURE-FREE BASIS.

Material.	Moisture.	Soluble sulfates.	Volatile sulfur.	Soluble unoxidized sulfur.	Insoluble unoxidized sulfur.	Sum of various forms.	Total sulfur determined on green material.	Total sulfur determined on dried material.	Sulfur lost by drying.
Rutabagas, green 1	89.0	0.328	0.093	0.373	0.073	0.867	0.964	0.749	0.215
Rutabagas, green 2	88.9	0.248	0.098	0.293	0.103	0.644	0.717	0.590	0.127
Rutabagas, green 3	89.8	0.276	0.106	0.235	0.088	0.695	0.736	0.583	0.153
Rutabagas, green 4	90.1	0.327	0.087	0.256	0.098	0.768	0.784	0.657	0.127
Average	89.5	0.295	0.096	0.289	0.091	0.744	0.802	0.643	0.155
Cabbage, green	94.3	0.195	0.077	0.409	0.111	0.792	0.818	...	...
Sugar beets	74.3	0.018	..	0.015	0.020	0.053	0.053	0.047	0.006
Sugar beet tops, green	85.6	0.052	0.0031	0.183	0.165	0.403	0.433	...	...
Alfalfa hay	10.8	0.179	..	0.075	0.108	0.362	0.361	0.346	0.015
Alfalfa, green	77.5	0.003	0.0066	0.151	0.124	0.282	0.288	...	...
Dried rape (*a*)	..	0.051	..	0.193	0.075	0.319	0.422	...	...
Dried rape (*b*)	..	0.000	..	0.106	0.071	0.177	0.160	...	...
Dried rape (*c*)	..	0.600	..	0.200	0.076	0.876	0.940	...	...
Dried rape (*d*)	..	0.304	..	0.253	0.078	0.635	0.794	...	...
Radishes, green (*b*)	89.1	0.000	0.010	0.090	0.009	0.109	0.173	0.139	0.034
Radishes, green (*d*)	85.8	0.420	0.038	0.230	0.146	0.834	0.820	0.749	0.071
Clover, green (*b*)	65.6	0.000	0.004	0.024	0.092	0.120	0.112	0.120	0.008
Clover, green (*d*)	76.4	0.071	0.014	0.093	0.063	0.241	0.235	0.214	0.021
Clover, green (*e*)	80.0	...	0.0055	...	...	...	...	...	...
Clover, green (*e*)	79.5	...	0.0035	...	...	...	...	...	...
June grass (*e*)	72.2	...	0.0022	...	...	...	...	...	...
Milk	87.0	...	0.037	...	...	...	...	...	...
Oats (grain)	..	...	Trace	...	...	...	...	...	...
Wheat (grain)	..	...	Trace	...	...	...	...	...	...

(*a*) No fertilizer added to soil in greenhouse.

(*b*) Nitrogen, phosphorus and potassium added to soil in greenhouse.

(*c*) Nitrogen, phosphorus and potassium and sodium sulfate added to soil in greenhouse.

(*d*) Potassium, nitrogen, phosphorus and calcium sulfate added to soil in greenhouse.

(*e*) Sample taken from field.

TABLE II.—DISTRIBUTION OF THE SEVERAL FORMS OF SULFUR IN PERCENTAGES OF THE TOTAL SULFUR FOUND.

Material.	Soluble sulfate. A.	Volatile sulfur. B.	Total soluble sulfur. C.	Insoluble sulfur. D.	Sum of fractions. B, C & D.	Loss on drying.	Total unoxidized sulfur. (C−A)+D.
Rutabagas, average 4 samples	37	12	73	11	96	19	47
Cabbage	24	9	74	15	98	..	65
Sugar beets	34	..	62	38	100	11	66
Sugar beet tops, green	12	1	55	38	94	.	...
Alfalfa hay	50	..	70	30	100	4	50
Alfalfa, green	1	2	52	43	97	.	...
Rape, dried (*a*)	12	..	58	18	76	..	64
Rape, dried (*b*)	00	..	61	44	105	..	105
Rape, dried (*c*)	64	..	85	8	93	..	29
Rape, dried (*d*)	38	..	70	10	80	..	42
Radishes, green (*b*)	00	6	52	40	98	20	92
Radishes, green (*d*)	51	5	80	18	103	9	47
Clover, green (*b*)	00	4	21	82	107		103
Clover, green (*d*)	30	6	70	27	103	9	67
Wheat (grain)	Trace	..	..	..	..	..	..
Oat (grain)	Trace	..	.	..	.	..	...

(*a*) No fertilizer added to soil.

(*b*) Potassium, nitrogen and phosphorus added to soil.

(*c*) Potassium, nitrogen and phosphorus and sodium sulfate added to soil.

(*d*) Potassium, nitrogen, phosphorus and calcium sulfate added to soil.

In Table II we have the different amounts of sulfur found, calculated to show the distribution of this sulfur, *i. e.*, what part of the total sulfur exists in these various forms. A study of this table shows that in the case of rutabagas, about 11% of the sulfur exists in the form of volatile sulfur, 37% as sulfates, and about 48% as unoxidized sulfur. In the case of sugar beets no volatile sulfur was determined, as none was believed to exist there. The correctness of this assumption may be questioned, however, in view of what was found later in the case of clover, grass and sugar beet tops. Alfalfa hay contains one-half its sulfur in the form of sulfates, about one-fifth soluble unoxidized sulfur, and the remainder, three-tenths, as insoluble unoxidized sulfur.

The four samples of dried rape were grown in the greenhouse by other members of the department, and form part of a great many experiments to observe the influence of sulfur fertilization on various crops. Rape sample (*a*) was the yield from a box of normal soil; sample (*b*) this same soil fertilized with potassium, nitrogen and phosphorus; samples (*c*) and (*d*) the complete fertilizer reinforced with sodium sulfate and calcium sulfate, respectively.

It is noticeable that where the rape, radishes and clover had only the residual sulfur in the soil to draw upon, but had an abundant supply of nitrogen, phosphorus and potassium and made vigorous growth, there were no sulfates in the tissues. Evidently the plants were utilizing all the available sulfur to form volatile sulfur compounds and build sulfur-containing tissue, and had none left as sulfates. Where sulfates were added to the soil, large quantities, 40–60%, were circulating in the plants as sulfates, and an abundant supply existed for building tissue and forming the volatile compounds of the plant.

It is important to notice (Table I) that where no sulfates had been added to the soil, the actual quantity of volatile sulfur found was only about one-fourth as much as where sulfates had been added. In the case of radishes (*b*) the volatile sulfur amounted to 0.010% and with sulfates added to the soil this rose to 0.038%. The figures for clover, under the same treatment, were 0.004% and 0.014%, respectively. The question may be properly asked as to whether this constituent of the plant is raised or lowered by a larger or smaller supply of sulfates in the soil. This increase of volatile sulfur on addition of sulfates does not appear in Table II, because here the very large amount of sulfates makes the percentage of volatile sulfur about the same in both cases. For a correct view of the matter, Table I must be examined.

An entirely unexpected discovery of volatile sulfur was made in the case of clover. So far as we are aware, no mention of a volatile sulfur compound in clover has been made in the literature. This seemed such a surprising result that to verify it determinations were made upon two samples of red clover from the field and upon grass (Kentucky blue grass). Several months later green alfalfa, sugar beet tops, cabbage and milk, were also examined for volatile sulfur. In every case volatile sulfur was found. Every precaution was taken to prevent the accidental entrance of any volatile sulfur into the drying apparatus. Potassium dichromate was added to the concentrated sulfuric acid to oxidize any sulfur compounds existing in the air that might pass through the first potassium hydroxide bottle. Another bottle of strong potassium hydroxide was placed between the sulfuric acid bottle and the drying tube to preclude the possibility of any volatile sulfur, given off by the acid, from passing into the drying tube. After all these precautions, volatile sulfur was found in these later determinations. As a further test for the correctness of these results, the apparatus with about 25 cc. of distilled water in the drying tube was run for eleven hours and no sign of sulfates was found. Two sources of this volatile sulfur seem possible: the existence in the material of some compound similar to the mustard oils or the splitting off from the proteins of volatile sulfur, as hydrogen sulfide. It would seem rather improbable that by drying below 100° proteins would give off a volatile sulfide yet that seems to be the most probable explanation, in view of the results secured by Rettger[24] and other investigators, who showed that, when milk was heated to 85°, lead acetate paper was blackened when held in the vapors. From experiments made in this laboratory it was found that the amount of this volatile sulfur is considerable, 50 mg. barium sulfate being obtained on drying 300 cc. of fresh milk. Casein precipitated with acetic acid and washed free from acid, on drying in the tube gave about 20 mg. of barium sulfate from 250 g. of casein.

Summary.

1. A widespread interest in the question of sulfur from both a theoretical and agricultural point of view is evident. Numerous investigations show many new compounds, either synthetic or natural, that contain sulfur. The use of sulfur or its salts as a fertilizer, and the requirements of the plant and the soil supply of this element, are subjects of interest and investigation.

2. The determination of the volatile sulfur, sulfates, soluble unoxidized sulfur, and insoluble unoxidized sulfur in seventeen samples comprising seven kinds of plant material is given.

3. A new method for determining volatile sulfur in plants is described. The material is dried in a tube with sulfur-free air, and the gases passed over heated copper oxide and oxidized. With small quantities the sulfur is all fixed as copper sulfate.

4. The volatile sulfur in field samples of rutabagas and cabbage averages about 10% of the total sulfur. In radishes and clover grown in the greenhouse, the amount present is dependent on a liberal supply of sulfates, being four times as great with added sulfates as without them.

5. Volatile sulfur is lost on drying green material in the steam oven. In field samples of rutabagas this amounted to 20% of the total. On greenhouse samples this amounts to from 10-20%.

6. Volatile sulfur was obtained from red clover, alfalfa, June grass and sugar beet tops not known to contain any bodies yielding such compounds. The volatile sulfur in milk was also determined. The nature of this compound is not known. In rutabagas it is evidently of a sulfide form, as silver sulfide is obtained when silver nitrate is added to the distillate from rutabagas.

7. The sulfates in the field samples examined varied from 10 to 50% Where large quantities of sulfates were added to the soil, there was a corresponding increase of sulfates in the plant tissue. Rape, radishes and clover grown in the greenhouse on soils low in sulfur, but supplied with

an abundance of nitrogen, phosphorus and potassium contained no sulfates.

8. Where no sulfates were added to the soil, 90% or more of the total sulfur was found in the form of unoxidized sulfur, probably in proteins. In the normally grown plants examined this was from 50–65% of the total. The plant was evidently very economical of its supply and made healthy, vigorous growth where no sulfates could be found in the tissue.

To Prof. E. B. Hart, at whose suggestion this work was undertaken, the author wishes to express thanks for his interest and encouragement.

BIBLIOGRAPHY.

(1) *J. Biol Chem.*, **9**, 439–462 (1911).
(2) *J. Chem. Soc.*, **99**, 2336 (1911)
(3) *J. Biol. Chem.*, **13**, 463 (1913).
(4) *Crells. Anal.*, **2**, 38, 68, 136 1790 (1799).
(5) Berzelius, *Jahrb.*, **6**, 242; **12**, 263.
(6) *Ann. chim. phys.*, II, **44**, 214 (1830); II, **53**, 181 (1833)
(7) *J. prakt. Chem.*, **19**, 218; *Pogg. Ann.*, **49**, 340.
(8) *Ann.*, **125**, 257.
(9) *Ber.*, **30**, 2332 (1897); *Chem. Zentr.*, II, 922; *Arch. Pharm.*, **235**, 44.
(10) *J. Pharm* , **27**, 39; *Ann.*, **34**, 223.
(11) Van Rijn, "Die Glykoside," pp. 183–198.
(12) *Arch. Pharm.*, **240**, 161 (1902).
(13) *Pharm. Post.*, **27**, 33.
(14) *Chem. Zentr.*, **75**, I, 1461 (1904).
(15) *Ibid.*, **81**, I, 375 (1910).
(16) *Z. anal. Chem.*, **30**, 661; *Landwirt. Vers. Sta.*, **41**, 176.
(17) *Arch. Pharm.*, **240**, 161.
(18) *26th Ann. Rept.*, **1903**, *N Car.*, p. 70.
(19) This Journal, **35**, 1628 (1913).
(20) *Ibid.*, **33**, 549 (1911); Wis Expt. Sta. Research, *Bull.* 14.
(21) Ky. Agr. Exp. Sta., *Bull.* 174 (1913).
(22) Mazières, *Le Engrais*, June 23, 1911; Boulanger, *Compt. Rend. Hebdom.*, Feb. 5, 1912, July 22, 1912; Demolon, *Compt. Rend. Hebdom.*, Feb. 19, 1912; Chaucrin and Desriot, *Journ. D'Agric. Prat.*, Mar 12, 1912; Vercier, *Prog. Agric. et Vit.*, Nov. 1, 1912.
(23) *Biochem. Z.*, **29**, 429–438.
(24) *Am. J. Physiol.*. **6**, 450 (1902).

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A METHOD FOR THE DETERMINATION OF FAT IN MILK (NEPHELOMETRIC METHOD).

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The methods for the determination of fat in milk, in common use at the present time, may be roughly classified as follows:

(1) Rapid methods, like the Babcock and Gerber methods, which de-

pend on the separation of the fat by centrifugation after treatment of the milk with reagents which alter the protein constituents. The separated fat is collected into a narrow portion of the vessel and the amount of fat determined by the length of the fat column.

(2) Methods like the Rose-Gottlieb-Farnsteiner and Meigs methods which depend on the direct extraction of the fat from the milk with fat solvents and determination by weighing the extracted material.

(3) Methods like the Adams' which depend on the extraction and weighing of fat from the milk after drying on fat-free filter paper or sand.

The method to be described is based on a new principle—the determination of the fat by comparison of the light reflecting power of a watery suspension of the milk fat with that of a similar suspension of a standard fat (triolein), making use of the nephelometer. The watery suspension is obtained by flocking a colloidal solution of the fat with an electrolyte (hydrochloric acid has been found most suitable). The colloidal solution is produced by mixing an alcoholic solution of the fat with distilled water. The same principle has been made the basis of a method for the determination of fat in blood.[1]

The nephelometric method possesses the advantage that it requires only a very small amount of milk—ordinarily 1 cc.—and should therefore be of special value in working with human milk or with that of small animals where it is inconvenient or impossible to obtain enough for the ordinary determinations. The time required is not greater than that needed for the "rapid" methods, while the accuracy is limited only by the accuracy of the instruments. The nephelometer is simple both in principle and construction and, while but little known at present, promises to come into general use, since it appears to be applicable to most quantitative uses, especially in the accurate determination of small amounts of material.

The procedure is as follows: One cubic centimeter of the milk, measured with an accurate pipette, is run slowly and with stirring into about 80 cc. of an alcohol-ether mixture (containing 3 parts of redistilled alcohol and 1 part of redistilled ether), in a 100 cc. graduated flask. (The measurement may be checked by determining the weight of the added milk.) The mixture is raised to boiling by immersion in a boiling water bath, cooled to room temperature, made up to 100 cc. with the alcohol-ether, shaken and filtered. The filtrate is clear and almost colorless.

For the determination, 5 cc. of the solution are run from a pipette, slowly with stirring, into 100 cc. of distilled water in a beaker, producing a slightly opalescent colloidal solution. The point of the pipette must be kept below the surface of the liquid during the outflow. A similar solution is prepared with 5 cc. of the standard fat solution (see below). To the standard and to the test solutions are added, simultaneously, 10 cc. portions of dilute (10%) hydrochloric acid and, after stirring, the solutions allowed to stand for five minutes, after which they are transferred to the comparison tubes of the nephelometer.

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[1] Bloor, *J. Biol. Chem.*, 17, 377 (1914).

For the comparison, the two tubes, filled to the same height with the solutions, are placed in the nephelometer with the standard tube always on the same side. If bubbles appear in the walls of the tubes they are removed by inverting two or three times. The movable jacket on the standard side is set at a convenient point, generally 50 mm. (Richards' nephelometer), and comparisons made by adjusting the jacket on the test solution until the images of the two tubes show equal illumination. At least five readings are taken, alternately from above and below, and the average taken as the reading. This reading is corrected from the calibration curve of the instrument and the fat value of the milk calculated from the corrected reading.

The standard solution used is an alcohol-ether solution of pure triolein, made with freshly distilled absolute alcohol and pure dry ether, of which 5 cc. contains about 2 mg. of fat.

Remarks on the Procedure.—The application of the nephelometric principle and the use of the Richards' nephelometer in the determination of fats have been discussed in a previous paper[1] and only the points essential to the use with milk will be mentioned here.

The Extraction.—The solvent combines the penetrating power of alcohol with the greater solvent power of ether. Running the milk slowly into the solvent which is kept in motion, causes the precipitation of the proteins in a finely divided flocculent form—in excellent condition for extraction. Under these conditions the presence of the great excess of solvent and the short heating is adequate for complete extraction.

The Standard.—The choice of triolein is empirical, triolein being readily obtainable of a good degree of purity.

Choice of Time for Comparison.—Both the triolein and the milk fat solutions change (decrease) slowly in value after the addition of the precipitant. The rate of change is, however, practically the same in both for a period of an hour or more, so that if the precipitating acid is added to both simultaneously, the readings may be made at once. Ordinarily, however, about five minutes is given to allow for slight differences in the time of addition of the acid.

The Nephelometer—Calibration.—A form[2] of the Richards' nephelometer[3] was used. It was found that the addition of a rack and pinion to the jacket on the comparison side was a great convenience. Matched test tubes are used for comparison tubes and as it was not possible to find two tubes which, when filled with the same solution, would give the same readings on both sides of the instrument, the tubes were marked and always used on the same side, the one used for the standard solution being on the left. The average of many readings of the right hand tube was then taken as the potential height of the standard.

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[1] Bloor, *Loc. cit*

[2] Made by the International Instrument Company, of Cambridge Mass.

[3] T. W. Richards, *Z anorg. Chem.*, 8, 269 (1895); Richards and Wells, *Am. Chem J*, 31, 235 (1904).

Lacking a nephelometer, many colorimeters may be adapted for the purpose, as has been shown by Kober[1] with the Duboscq colorimeter, and the author with the Schreiner[2] instrument.

Since the amount of light reflected is not exactly proportional to the depth and fat value of the solutions (because of different distances of the reflecting surfaces from the eye, absorption of light by the upper layers of liquid, different rates of flocking in solutions of different concentration, etc.), it is necessary to calibrate the nephelometer for different strengths of test solution, and for different standards, if more than one is used. The values obtained are plotted on a curve and corrections in the readings made from it.

Again, since the total light reflected from a given depth of solution depends as well on the size of the suspended particles as on their number, it is obvious that success with a nephelometric method depends on keeping as constant as possible those physical and chemical conditions which influence the aggregation of the particles. The concentration of alcohol-ether and acid, the rate of addition of the alcoholic fat solution, etc., should be the same; also the solutions to be compared should not be too far different in value, since strong colloidal solutions flock more quickly than weak ones. (Readings above 70 mm. and below 30 mm. with the standard at 50 mm. are rejected.)

The calibration of the nephelometer for a given standard is carried out as follows: Suspensions of triolein of various known values are prepared as in the method, and compared with the similarly prepared standard triolein suspension in the nephelometer, with the movable jacket on the standard set as its usual place. The readings obtained are compared with the theoretical readings for the different values and the correction for each strength of solution determined. From these values a curve is plotted, from which intermediate values are obtained. In general, it is found that suspensions stronger than the standard give readings higher (*i. e.*, lower fat values) than the theoretical, and solutions weaker than the standard give lower readings, indicating that probably the greater speed of flocking in the stronger solutions is the main factor in the abnormal readings.

Correction for Reagents.—When freshly distilled alcohol and ether are used it is not ordinarily necessary to make any correction for reagents.

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[1] Kober, *J. Biol. Chem.*, 13, 485 (1913).

[2] Bloor, *Proc. Am. Chem. Soc.*, Rochester, 1913.

Results.—Duplicate determinations made on the same milk agree with one another within the limits of error of the instrument (about 3%).

In the table below comparison is made of values obtained by the nephelometric method, the Babcock method and also in some cases, the Adams' method. In using the Babcock method, a calibrated pipette and specially prepared bottles were used. The cows' milk was mixed dairy milk collected from various sources. The human milk was from patients in the obstetric division of the Washington University Hospital, for which I am indebted to the kindness of Professor Henry Schwarz and Doctor Q. U. Newell. The samples were from cases in various early stages of lactation and were selected so as to obtain as wide range of fat values as possible.

TABLE I.—COMPARISON OF RESULTS OBTAINED BY THE NEPHELOMETRIC AND OTHER METHODS FOR FAT IN MILK.

Milk sample.	Babcock.	Nephelometric.	Adams (Soxhlet).
R. Kingston, Can	2.9	2.85	..
B. Kingston, Can	3.1	3.00	..
Hospital supply I., St. Louis, Mo	3.5	3.6	..
U. D. I., St. Louis, Mo	3.0	3.1	3.01
Hospital supply II, St. Louis, Mo	3.0	3.1	.
M. Kirkwood, Mo	3.6	3.8	3.80
J. A., St. Louis, Mo	3.5	3.6	3.77
Human milk.			
I. L. 22 days post partum	4.7	4.8	4.70
II. V. 10 days pp. (child still-born)	8.2	8.1	.
III. W. 11 days pp	3.9	3.83	..
IV. G. 4 days pp	3.75	3.8	..
V. N. 3 days pp. (colostrum)	3.3	3.4	..
VI. M. 16 days pp	2.0	2.2	2.15
VII. B. 8 days pp. (breast caked a little)	5.6	5.60	5.71

The preliminary work on this method was done in the Gordon Hall Laboratories of Chemistry of Queens' University and in the Kingston Dairy School at Kingston, Canada, and I wish in conclusion to express my appreciation of the kindness of Professor W. L. Goodwin, of the University, and of Mr. Zufeldt, Director of the Dairy School, in placing at my disposal the facilities of these institutions.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

NEPHELOMETRY IN THE STUDY OF NUCLEASES.[1]

BY PHILIP ADOLPH KOBER AND SARA S. GRAVES.

Received April 8, 1914.

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[1] Read at the Cincinnati Meeting, Am. Chem. Soc., April, 1914.

C. Interfering Substances; D. Technic; E. Applications to Physiological Material. III. Summary.

I. Introduction.

The study of nucleases has been hindered by the lack of suitable technic. Walter Jones[1] writes: "It's somewhat difficult to decide whether or not a ferment has brought about the decomposition of a nucleic acid, unless the decomposition is complete. The methods for the recovery of the undecomposed nucleic acids are so poor that one cannot always decide whether a partial disappearance of the substance is due to ferment action, or to analytical error."

It is the object of this paper to describe a new method for estimating undigested nucleic acids. Essentially, the method consists in adding a precipitant to a dilute solution of the nucleic acids and estimating the resulting suspensoids, nephelometrically. The results with yeast nucleic acid alone are given in this paper.

II. Method.

A. Precipitant for Nucleic Acids.—As strong hydrochloric acid in aqueous and alcoholic solutions has heretofore been used in the preparation of nucleic acids, attempts were made to use it as a nephelometric precipitant.[2] As the suspensoid gelatinized appreciably, it did not seem stable enough for quantitative work. Next, experiments were made, using dilute solutions of certain proteins, *i. e.*, casein and edestin[3] as precipitants.

Nucleic acids, as is known, combine in slightly acid solutions with proteins to form artificial "nucleins."[4] This reaction, preliminary qualitative experiments showed, was given by one part of yeast nucleic acid in a million parts of water. After considerable work, these two proteins were abandoned because uniform results were not obtained. The probable reason is that for the quantitative formation of these "nucleins" a certain concentration of hydrogen ions is necessary, which is too near the precipitation point of the proteins to be nephelometrically applicable. Therefore, a protein soluble at that hydrogen ion concentration was next sought. Egg white, which seemed to have this property, was tried and found satisfactory.

B. Experimental Work. (1) Preparation of Egg Albumin.—As commercial dried egg albumin was not completely soluble in water, albumin from eggs—in most cases not over 48 hours' old—was used. The egg white showed a slight turbidity after diluting to a 1% solution, but, upon shaking with 0.1 *N* acetic acid, a precipitate, probably a globulin, was thrown down and after filtration a clear solution was obtained. The amount of 0.1 *N* acetic acid necessary for the complete removal of this interfering precipitate was determined by the following experiment: 15 g. of egg white were shaken with 5, 7, 9, and 11 cc., respectively, of 0.1 *N* acetic acid; water was added to make 1% solutions which were then filtered, and the turbidity determined by comparing in the nephelometer with distilled water set at 15 mm. The following results were obtained:

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[1] *J. Biol. Chem.*, **9**, 130 (1911); also Levene and Medigreceanu, *Ibid.*, page 65.

[2] For the definition of "Nephelometric Precipitant" see THIS JOURNAL, **35**, 1585 (1913).

[3] Reported at the Rochester meeting of the Am. Chem. Soc., September (1913).

[4] R. Altmann, *Archiv. Physiol.*, **1889**, 524; T. Milroy, *Z. physiol. Chem.*, **22**, 307 (1896–97).

0.1 *N* acid added. Cc.	Nephelom. reading. Mm.	Standard. Distilled water. Mm.
5	Heavy cloud	15 0
7	9.5	15.0
9	8.5	15.0
11	9.7	15.0

The variation of the readings being inappreciable, 7 cc. of acid were used—corresponding to 0.5 cc. of 0.1 *N* acetic acid per g. of egg white.

A clear 1% albumin solution was diluted and a 0.1% solution was found to give a suitable nephelometric curve with varying amounts of nucleic acids, but the reaction with some albumins took place slowly. To hasten the reaction and to insure an excess of precipitant a 0.2% solution was finally adopted.

It became evident, after obtaining several curves, that the alkalinity of the egg albumin varied considerably, and that additional acid was necessary to obtain a favorable hydrogen ion concentration. There being no rapid and accurate method for determining the alkalinity, varying amounts of acids were added and constants of the resulting curves determined by the means of the nephelometric formula, $Y = S/X - (1 - X)Sk/X^2$. For this purpose two points were found, usually the ratios of 1.0 and 0.70. To 250 cc. of 0.2% egg albumin were added 2, 2.5 and 3 cc., respectively, of 0.1 *N* acetic acid. The constants obtained with these amounts of acids for single eggs and for mixtures are given in the following tables:

Single eggs.	2 cc. 0.1 *N* acid. *k*.	2.5 cc. 0.1 *N* acid. *k*.	3 cc. 0.1 *N* acid. *k*.
I	0.23	0.24	0.25
II	0.13	0.16	0.13
III	0.33	0.36	—0.03
IV	0.28	0.12	0.17
V	0.30	0.17	0.25
VI	0.40	0.16	—0.04
Mixtures.			
I	0.38	0.18	—0.04
II	0.37	0.22	0.12
III	0.40	0.23	0.18
IV	0.31	0.30	0.25

(2) *The Use of Egg Albumin.*—The egg albumin solutions, although clear, have a tendency to form shreds on the surface of the liquid. These shreds increase considerably upon shaking. Therefore, like all solutions of colloids, these solutions must be used with caution.

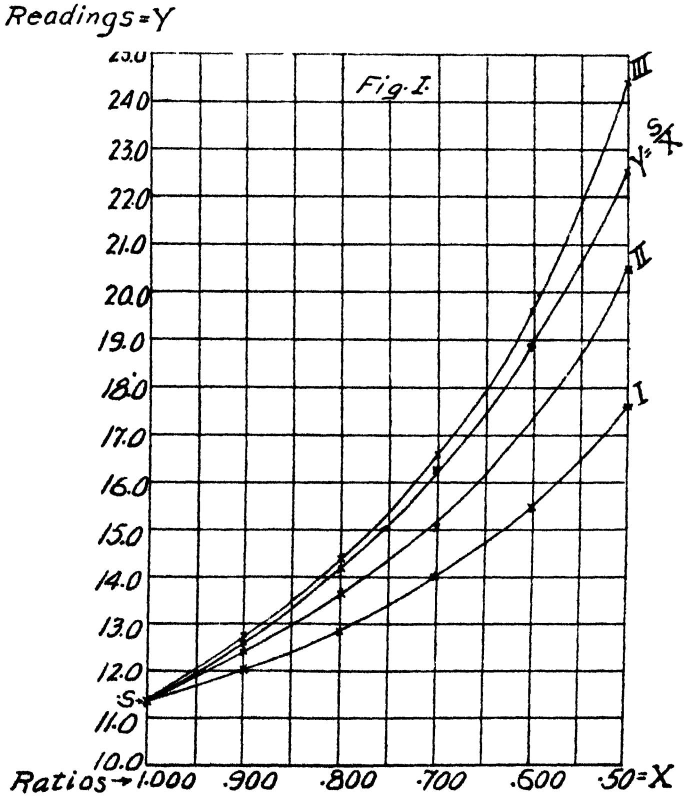
The formation of "nuclein" precipitates is strongly affected by hydrogen ions. This can be seen with a 0.2% egg albumin, which, without acetic acid, gives very little "nucleins," but on the addition of only 1 cc. of 0.1 *N* acetic acid to 50 cc. of albumin, the precipitation is complete.

The following results are typical of the readings and the curves obtained with albumins with varying constants:

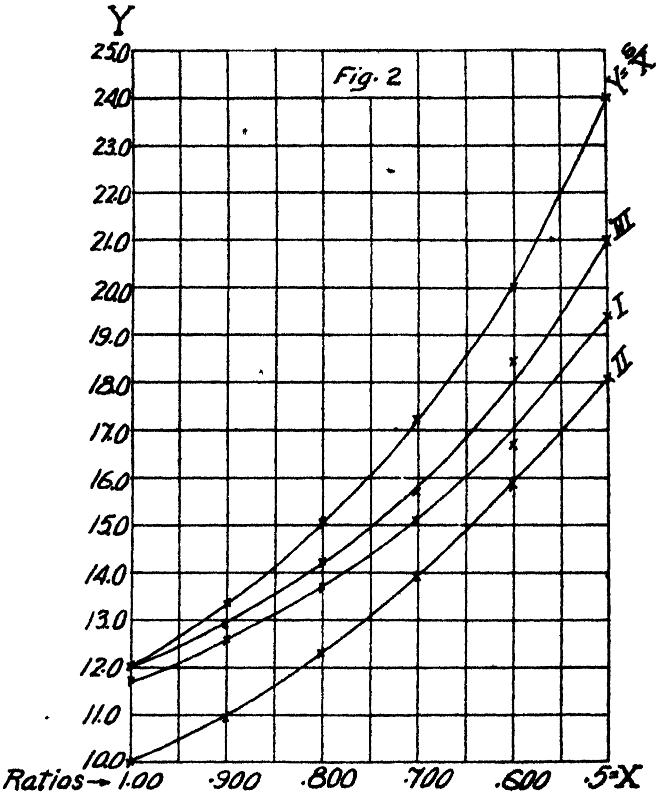
Curves.	Constant.	Ratio of sol.	1.0 mm.	0.9 mm.	0.8 mm.	0 7 mm.	0.6 mm.	0.5 mm.
I...............	0.34	.	11.4	12.0	12.8	14.0	15.5	17.6
II...............	0.24	..	11.2	12.2	13.5	14 9	..	20.3
III...............	—0.03	..	9.1	10.1	11.5	..	15.8	20.0

For the sake of comparison, Curves II and III were transposed to the same standard as I.

From Curve III it can be seen that the readings are higher than the hypothetical and therefore the conclusion can be drawn that, at least



in the more dilute solutions, the precipitation is not complete. From the curves it can also be seen that the greater the constant the greater the percentage error in determining the ratio of solutions, but it seems unlikely that a large constant (greater than 0.30) can be a normal nephelometric phenomenon.



To show the sensitiveness of the reagent, the following experiments were made:

Solution I.—1 cc. 0.1% nucleic acid was diluted to a liter, making 1 part in 1,000,000.

Solution II.—5 cc. 0.1% nucleic acid was diluted to a liter, making 1 part in 2,000,000.

Compared to distilled water in the nephelometer, the readings were as follows:

Standard.		Unknown.	
Solution.	Reading. Mm.	Solution.	Reading. Mm.
H_2O	20.0	H_2O	20.0
H_2O	20.0	I	7.0
H_2O	20.0	II	11.0
H_2O	20.0	Reagent	13.0

C. Interfering Substances.—The formation of "nucleins" being easily affected by hydrogen ions, ought to be influenced by almost any substance, since most substances change the hydrogen ion concentration of a solution. However, when diluted as is necessary for nephelometric work, an equal weight of substance ought to have no appreciable effect. This was actually found to be the case.

One part by weight of the substances given below was dissolved with one part of nucleic acid and the latter estimated nephelometrically. Within experimental error, the controls gave the same readings as these mixtures:

Inorganic: NaCl, $NaNO_3$, Na_2SO_4, $(NH_4)_2SO_4$, NH_4Cl, $BaCl_2$, $Ba(NO_3)_2$, NaH_2PO_4, $CaCl_2$, $NaC_2H_3O_2$, $KC_2H_3O_2$, $Ca(NO_3)_2$

Organic: Glycerophosphoric acid, Alanine, Tyrosine, Histidine, Asparagine, Phenyl alanine, Urea, Peptone, Ereptone, Dextrose, Levulose, Urine (assumed 5% solids), Stomach contents (assumed 5% solids), Extract of pancreas (dried)

D. Technic.—The albumin was obtained from egg white calculating it as 10% by weight. A 1% solution of egg albumin was made by roughly weighing the whites of from 4 to 6 strictly fresh eggs, shaking well with 0.1 *N* acetic acid (0.5 cc. per gram of egg white) diluting with 10 volumes of water (allowance being made for the original acid) and filtering twice. 50 cc. of the clear 1% solution were put into a flask, acetic acid added (usually 3 cc.) and made up to 250 cc. with distilled water. This 0.2% solution was used as a precipitant.

The nucleic acid solution was made by dissolving 0.1 g. of nucleic acid in 100 cc. of distilled water. This 0.1% stock solution was further diluted before using.

One volume (10 cc.) of nucleic acid (not stronger than 0.01%) was precipitated by running in from a pipet[1] two volumes (20 cc.) of 0.2% albumin solution. After shaking gently in a rotary fashion, the solution was ready for reading.[2] In most cases 0.007% nucleic acid was used as a standard.

E. Application to Physiological Material.—To show that this method is applicable in physiological work, normal specimens of urine, stomach contents and pancreatin were added to nucleic acid solutions and precipitates formed in the usual way. The following figures were obtained:

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[1] It is well to dip the point of the pipet below the liquid to avoid the entrance of air bubbles which sometimes cause agglutinations.

[2] The nephelometric tubes and plungers must be kept clean. In the nephelometers heretofore described the plungers and the receptacles for the nephelometric tubes were painted with asphaltum paint. As this paint is somewhat affected by alkaline and other solutions, it became necessary to avoid the use of paint on surfaces which came in contact with the solvents. By making the plungers of hollow glass and painting the interior sides and by making the receptacles of glass and painting them on the outside, this difficulty has been overcome. These new plungers also seem better adapted for the albumin solutions, as there is less tendency for the fibers and air bubbles to stick upon the plungers.

Mixtures.	k.	Ratio of sol.	1.0 mm.	0.9 mm.	0.8 mm.	0.7 mm.	0.6 mm.	0.5 mm.
I Urine and nucleic acid	0.23	...	11.7	12.6	13.7	15.1	16.7	19.4
II Pancreatin and nucleic acid	0.11	...	11.2	12.1	13.5	15.2	17.1	19.3
III Stomach contents and nucleic acid	0.19	...	12.0	12.9	14.2	15.7	18.5	21.0

These figures are the average of 5 or 6 readings. In addition to 0.05 g. of nucleic acid, solution I contained 2 cc. of urine; solution II 0.02 g. of pancreatin, and solution III 2 cc. of filtered stomach contents. As may be seen, the curves with the mixtures run practically the same as nucleic acid alone.

To determine the presence of nucleases and their relative activity, solutions of nucleic acid were incubated with pancreatin, and the digestion determined by comparing at intervals with known amounts of nucleic acids and precipitating in both cases with 0.2% solution of egg albumin.

Solution I.—Contained 0.05 g. of nucleic acid, 2.5 cc. of 2% pancreatin solution (Mercks) 2.5 cc. of 2% tricresol, made up to 50 cc. with distilled water. *Solution II* was made in the same manner, except that it contained 5 cc. of 2% pancreatin solution (Eimer & Amend).

NUCLEIC ACID DIGESTED.

Pancreatin.	0 time. Per cent.	1 hr. Per cent.	2 hrs. Per cent.	3 hrs. Per cent.	4 hrs. Per cent.	5 hrs. Per cent.
I Merck	0.0	38.0	65.0	75.3	76.8	78.3
II Eimer & Amend	0.0	21.5	28.5	33.0	(33.0)	41 5

III. Summary.

The nephelometer can be used for the study of digestion of yeast nucleic acid, when a 0.2% solution acid egg albumin is used as a precipitant. This reagent is not appreciably affected in dilute solutions by most substances met with in physiological work, and will easily detect one part yeast nucleic acid in 1,000,000 parts of water.

NEW YORK, N. Y.

A PROPOSED MODIFICATION OF THE KOBER METHOD FOR QUANTITATIVE AMMONIA DISTILLATION BY AERATION.

BY F. L. DILLINGHAM.

Received March 25, 1914.

The method outlined by P. A. Kober and S. S. Graves under the title, "Quantitative Ammonia Distillation by Aeration" in THIS JOURNAL[1] seemed of such great value that it was given a series of trials by the writer.

For this purpose ammonium sulfate, 99.80% $(NH_4)_2SO_4$, was used. The details of the method employed are as follows: A weighed quantity of ammonium sulfate was placed in a Kjeldahl flask of 800 cc. capacity and 20 cc. of concentrated sulfuric acid (1.84 sp. gr.) were added, followed by an addition of 80 cc. of distilled water. The mixture was cooled and the flask connected with an absorption bottle containing a slight excess of standard sulfuric acid. A suction pump was attached and air drawn through at a slow rate while 60–90 cc. of a saturated solution of sodium hydroxide were drawn into the Kjeldahl flask, which was given a rotary motion in order to cause thorough mixing of the solutions. In nearly every case the heat of neutralization was utilized. Air was then drawn through at a rapid rate.

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[1] THIS JOURNAL, 35, 1594 (1913).

The rate of aeration was determined by means of the apparatus suggested in the above mentioned paper (p. 1597). The most powerful pump at my disposal allowed a rate of only 360 liters of air per hour, which is a slower rate than that of pump *A* used by Kober and Graves; however, the authors state, on page 1598: "400 to 600 liters of air seems to be sufficient for the average amount of ammonia obtained in Kjeldahl work. If a weaker pump is used, or if larger quantities of ammonia are to be distilled, more aeration must be used." Consequently more aeration was employed in my experiments by carrying on the aeration for various lengths of time, ranging from one and one-half to five hours.

AMMONIUM SULFATE DETERMINED BY AERATION ALONE.

Amt. of $(NH_4)_2SO_4$ taken. G.	$(NH_4)SO_4$ equivalent to ammonia recovered by aeration alone. G.	Per cent.	Time of aeration. Hours.
0.2508	0.2286 =	91.16	1.5
0.2558	0.2154 =	84 21	1.5
0.2485	0.2088 =	84.03	3
0.2505	0.2180 =	97.02	4
0.2503	0.2247 =	89.77	5
0.2078	0.1790 =	86.14	1.5
0.2023	0.1810 =	89.47	1.5
0.2011	0.1863 =	92.65	1.5
0.4003	0.3713 =	92.76	3
0.4024	0.3793 =	94.25	2
0.3990	0.3873 =	97.06	4
0.4018	0.3410 =	84.87	3
0.4000	0.3555 =	88.87	2

A large number of determinations were made, and in no case could all the ammonia be recovered by this method of aeration. In each case quantitites of ammonia varying, in round numbers, from 3% to 15% were found to be retained in the residual liquid in the Kjeldahl flask. This was shown to be the case by titration of the excess of standard acid in the absorption bottle in the usual manner. In two instances aeration was carried on from four to five hours and here from 11% to 12% of the ammonia failed to be drawn over. The amount of ammonia in the residual liquid in the Kjeldahl flask was determined in one of two ways: by transferring the liquid to another flask and subjecting it to steam distillation, or by applying a low flame to the Kjeldahl flask and continuing the aeration for one hour longer. Either of these two ways allowed all of the ammonia to be recovered.

These results are at variance with those of the authors of the previously mentioned article, and I am unable to account for the large quantities of ammonia which remained in the residual liquid. Possibly under the conditions of the experiments, a double salt of ammonia is formed which fails to give up all of the ammonia by aeration alone. Possibly the lower rate of aeration may account for the failure. I hope to be able to investigate this point further.

This failure to recover all of the ammonia, by aeration alone, suggested a modification of the method has been carefully tried out and which it is desired to offer. The modification consists in utilizing the heat of neutralization and in heating the liquid in the Kjeldahl flask over a low flame during the entire period of aeration. Pieces of zinc may be added to prevent bumping. It is well also to use a larger amount of water than the original method calls for. The outlet tube of the Kjeldahl flask should be provided with a glass trap to prevent carrying over of the sodium hydroxide. This modification will allow all of the ammonia to be recovered from ammonia sulfate in one and one-half hours. The liquid in the absorption bottle naturally becomes quite hot from the steam, but no loss of ammonia occurs, provided the standard acid is present in excess. When the absorption of ammonia is complete the absorption bottle may be cooled and the excess of standard acid titrated in the usual manner.

AMMONIUM SULFATE RECOVERED BY MODIFIED METHOD.

Amt. of $(NH_4)_2SO_4$ taken. G.	$(NH_4)_2SO_4$ equivalent to ammonia recovered by aeration and heating. G.	Per cent.	Time of aeration. Hours.
0.2020	0 2015 =	99.76	1.5
0.2013	0.2009 =	99.80	1.5
0.4023	0.4017 =	99.86	1.5

It seems to me that this modification is of especial value in those instances where a powerful suction pump is not available, as the time of distillation by aeration can be shortened to one and one-half hours, or possibly less, by the application of gentle heat during the period of aeration.

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NOTE.

The Survival of Amylase in Dried Fodders.—The wide distribution of amylase in green plants is well known, and the literature on this subject has become quite extensive. No work seems to have been recorded, however, on the fate of this enzyme when the plant is subjected to the curing process common in agricultural practice. When the possible function of the plant amylase in the digestion of the feed by herbivorous animals is considered, a new interest attaches to the amylase content of the plant and the loss that occurs in curing. This paper presents a preliminary study of the amount of amylase present in four dried fodders, *viz.*, alfalfa hay, clover hay, timothy hay and corn stover.

The method used in this work is based upon the new gravimetric method recently proposed by Sherman.[1] A crude enzyme preparation was obtained in the following manner: 200 g. of the finely ground fodder, about six months old, were allowed to remain in contact with 500 cc. water for one hour at a temperature not exceeding 15° C. The wet mass was then subjected to a pressure of 300 kg. per sq. cm. in a Buchner press. From 350–375 cc. of juice were recovered. Sufficient 95% alcohol was added to bring the alcohol concentration to 35%; a heavy flocculent precipitate resulted which was filtered off as rapidly as possible and rejected. To 350 cc. of the filtrate more alcohol was added until a concentration of 66% was reached. The resulting precipitate was filtered, washed with alcohol and ether and dried *in vacuo* over sulfuric acid. Further purification of the enzyme was not attempted.

The starch used in testing the saccharogenic power of the enzyme was Baker's soluble starch which had been further purified by the method of Ford[2] until a portion gave a clear solution in boiling water, and was practically neutral to rosolic acid. One-tenth of a gram of the enzyme powder was dissolved in 5 cc. water at 40° and added to 45 cc. of a starch solution of the same temperature and of such concentration that the mixture contained exactly 2% soluble starch. The mixture was kept at 40° for one hour. At the expiration of that time 20 cc. of 0.1 *N* NaOH was added to inhibit further enzyme action and the volume made up to 100 cc. with distilled water. The saccharogenic power was found by determining the reducing power of 25 cc. of this solution by Allihn's method. The results are set forth in the following table.

	Enzyme preparation.			
Source.	Amount obtained, g.	Amount used, g.	Total maltose formed, g.	Saccharogenic power.
Alfalfa hay I	1.6	0.1	0.427	4.27
Alfalfa hay II	1.9	0.1	0.400	4.00
Clover hay	2.4	0.1	0.181	1.81
Timothy hay	1.6	0.1	0.043	0.43
Corn stover	1.2	0.1	0.019	0.19

Recalculating these results into terms of amylolytic activity of 100 g. of the dry fodder, the following figures are obtained:

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[1] This Journal, 32, 1073 (1910).

[2] *J. Soc. Chem. Ind.*, 23, 414 (1904).

Fodder.	Saccharogenic power of 100 g.	Fodder.	Saccharogenic power of 100 g.
Alfalfa hay I	7.67	Timothy hay	0.77
Alfalfa hay II	8.50	Corn stover	0.26
Clover hay	4.88		

These figures represent of course minimal values, since a slight loss of enzyme might be expected to occur in each step of the process of preparation. The addition of sodium phosphate and sodium chloride as electrolytes failed to increase the activity, probably because electrolytes were abundantly present in the crude enzyme preparations. It is interesting to note, however, that the fodder retains some amylolytic activity after drying and that this activity is roughly proportional to the number of living cells in the plant at the time of cutting. RAY E. NEIDIG.

CHEM. SECTION, IOWA AGR. EXPT. STATION,
AMES IOWA

NEW BOOKS.

Chemistry in America. Chapters from the History of the Science in the United States. By EDGAR F. SMITH, Blanchard Professor of Chemistry, University of Pennsylvania. Illustrated. D. Appleton & Company: New York and London. 1914. pp. 356 + xiii. Price, $2.50.

The appearance of this book brings to mind an address by Professor Benjamin Silliman on "American Contributions to Chemistry," which was delivered in August, 1874, at Northumberland, Pa., on the occasion of the celebration of the Centennial of Chemistry, at the grave of Priestley. Dr. Smith has, however, brought to light much matter that was apparently not discovered by Silliman and, by quoting the authors whose work be describes, he is able to give a clearer idea of the nature and value of this work. It must be confessed that most of the chemical publications to which attention is called are of little value and have naturally been forgotten.

It is nevertheless interesting to learn that the earliest contribution to chemistry from this country appeared September 10, 1768, in the Transactions of the American Philosophical Society. The title is "An Analysis of the Chalybeate Waters of Bristol in Pennsylvania." The author is Dr. John de Normandie. Liberal quotations from the article are given which show that the author used the balance. Then follow quotations from an article by James Madison, who was Professor of Chemistry and Natural Philosophy at William and Mary College as early as 1774, and from an article by Dr. Robert McCauslin. The author of the book then remarks: "These communications testify to a spirit of inquiry, at least, on the part of our early devotees to science. They are, further, interesting in that they show the use of the balance as early as 1768 and indicate the steps of analysis."

In 1792 James Woodhouse founded the Chemical Society of Philadelphia. "As far as can be learned, Woodhouse was its first and only president. This Society lived about seventeen years. Its members favored Lavoisier's doctrine of combustion." It appears that "every year an address was delivered before the Society." Two of these addresses are given in full—one by Thomas P. Smith, delivered in 1798, and one by Felix Pascalis in 1802.

"The arrival of Joseph Priestley in America, in 1794, and his frequent presence among the men of science of that day, greatly stimulated scientific studies." Considerable space is given to matters pertaining to him, including the eulogium delivered after his death.

Thomas Cooper, professor at Dickinson College, and afterwards at the University of Pennsylvania, was the first one to make metallic potassium in this country. He was also the editor of Thomas Thomson's "System of Chemistry."

In 1801 Robert Hare communicated to the Chemical Society of Philadelphia a description of the oxy-hydrogen blowpipe which afterwards came to be known as the compound blowpipe. His description of this valuable piece of apparatus is contained in his "Memoir of the Supply and Application of the Blowpipe, containing an account of the new method of supplying the Blowpipe either with common air or oxygen gas; and also of the effects of the intense heat produced by the combustion of the hydrogen and oxygen gases." Of this Dr. Smith justly remarks, "It is a real landmark in scientific discovery." Hare was only twenty when he invented the blowpipe. He later became professor in the University of Pennsylvania, which position he held until his resignation in 1847. He was without doubt the most influential chemist of that time in America.

Without going into further details, reference may next be made to James C. Booth, the first American to study analytical chemistry in Germany. "With an education probably unequalled at that time by any chemist in America, he returned to the United States, and, in 1836, established in Philadelphia a laboratory for instruction in chemical analysis and applied chemistry." A little later T. Sterry Hunt (1826–1892) appeared on the scene. In regard to him, Dr. Smith says: "An active participant in the upbuilding of chemistry in America was T. Sterry Hunt." J. Lawrence Smith (1818–1883) was active at about the same time. His paper on a method of analyzing silicates by the use of calcium carbonate and chloride "was a very valuable contribution to analytical methods." His principal work had to do with meteorites.

Frederick A. Genth (1820–1893) was a German. He came to this country in 1848. After "conducting a laboratory for commercial analysis and the instruction of special students in chemistry, he became Professor of Chemistry in the University of Pennsylvania, in 1872. "His earliest contributions were upon geological subjects. Later he devoted much time to mineralogical problems. The chemical research by which he is best known to chemists relates to the ammonia cobalt bases (the cobalt-ammines) developed jointly with Wolcott Gibbs. His original memoir was published in 1851 and contained the first distinct recognition of the existence of perfectly well defined and crystallized salts of the ammonia cobalt bases. The joint monograph of Genth and Gibbs appeared in 1856. This elaborate and extended research has always stood among the finest chemical investigations ever made in this country."

"Wolcott Gibbs (1822–1908) for years held the most commanding position among the chemists of the United States."

"It was Gibbs' peculiar merit, that he, more than any other man, introduced into the United States the German conception of research as a means of chemical instruction." His investigations covered a wide range of subjects in inorganic, analytical, organic, and physical chemistry. "It was in the great research upon the ammonia cobalt bases, to which reference has already been made, that Gibbs finally found himself."

His most important contribution to analytical chemistry was the electrolytic determination of copper now universally used. "The entire field of electro-analysis was thus thrown open by him." His remarkable series of researches upon the complex inorganic acids, the publication of which began in 1877, continued well into the nineties.

Gibbs undoubtedly exerted a powerful influence upon the development of chemistry in this country. His sympathy with young men, his enthusiasm, his absolute fidelity to the highest ideals deeply affected many a young worker and helped to hold him on a true course.

Others whose work is discussed in the book before us are Albert Benjamin Prescott, Samuel W. Johnson (1830–1909) a pioneer in Agricultural Chemistry, John W. Mallet (1832–1912) of the Univeristy of Virginia, M. Carey Lea (1823–1907), and Josiah Parsons Cooke (1827–1894) of Harvard.

The book closes with some account of J. Williard Gibbs (1839–1903), of Yale, whose contributions to physical chemistry "are fundamental in nature and of broad application."

Dr. Smith has wisely refrained from speaking of those who are still living. In conclusion he says: "It is not the writer's purpose to discuss the investigations which have come from the many working centers of the United States during recent years, that story awaits another narrator; but, if only a desire, on the part of Americans to learn more concerning the place which American chemists occupy in the world's history of chemistry, is awakened, this compilation of facts will not only have been a pleasure but it will have served a worthy purpose."

The book is to be regarded as a "compilation" and not as a history. All American chemists should be thankful to the author for the pains he has taken to collect this material and for placing it before us. It furnishes

the basis for the history of chemistry in America which remains to be written.
IRA REMSEN.

Chemical German. By FRANCIS C. PHILLIPS. The Chemical Publishing Co., Easton London: Williams and Norgate. pp. xii + 241. Price, $2.00.

"The work is intended for students who have had at least a year of German and who have mastered the elements of chemistry" (preface). This is not a book of the old style on "Scientific German" in general, but a systematic work designed to give the student an apportunity thoroughly to master the German language of chemistry. The first fifty pages include reading exercises involving chemical nomenclature in the restricted sense, as well as the language used in discussing familiar laboratory operations. These are followed by quotations from various authors dealing with topics in the history of chemistry and with a multitude of specific subjects, both descriptive and theoretical. The book concludes with an excellent vocabulary, which, in addition to strictly technical words, includes also the exact English equivalents of *ordinary* German words when the latter are used in chemical connections (a case in which the dictionary often confuses instead of helping the student). The book is compiled with excellent judgment and will fulfil its purpose admirably.

ALEXANDER SMITH.

Annuaire pour l'An 1914. Published by the Bureau of Longitudes. Paris Gauthier-Villars 16mo. Price, $1^1/_2$ francs.

The physical and chemical tables of this yearly publication were described last year as fragmentary and unreliable. This year's installment is not as good as last year's.
J. W. R.

"Introduction to Higher Mathematics for Scientists and Physicians." By DR. J. SALPETER. Jena. Gustav Fischer, 1913. pp 336, with 147 figures and index Price, 13 marks, bound.

Several attempts have been made in recent years to make higher mathematics more palatable for those who dislike the extreme logical rigor so highly prized by the present-day mathematician, and more attainable by those who need in their professional work some acquaintance with the methods and results of higher mathematics. While granting the unique quality of the mental discipline afforded by the rigorous treatment of mathematical problems, the average student feels that after a considerable practice in such discipline he is entitled to a broader and more descriptive presentation of many of the more advanced theorems of mathematics than is to be found in most text-books. Mathematics is to a large degree an experimental science, and the methods of exposition which are customary in other experimental sciences may be applied with profit in this. That man who claimed that no one should lose a logarithm table who could not make one might equally well demand that no one should use a balance who could not construct one.

Dr. Salpeter, after experience in teaching higher mathematics to men not intending to become professional mathematicians, offers the present book as a compromise in which he attempts to attain the highest degree of rigor compatible with *Anschaulichkeit.* His problems are only occasionally chosen with reference to their immediate application to physical science, but he introduces two interesting chapters, one on the general methods of treating scientific problems mathematically, and one on the second law of thermodynamics.

The real value of such a book can only be tested by its actual use as a text, but the originaity shown by the author both in the arrangement of the material and in the detalis of presentation, must render this book an important contribution to the mathematical pedagogics.

GILBERT N. LEWIS.

Outlines of Theoretical Chemistry. By FREDERICK H. GETMAN, Ph.D. (Johns Hopkins) Associate Professor of Chemistry in Bryn Mawr College. New York: John Wiley & Sons, 1913. ix + 467 pp. Price, $3.50 net.

In the preface, Professor Getman writes: "The present book is designed to meet the requirements of classes beginning the study of theoretical or physical chemistry. A working knowledge of elementary chemistry and physics has been presupposed in the presentation of the subject. * * * * * With the exception of a few paragraphs in which the application of the calculus is unavoidable, no use is made of the higher mathematics." The nineteen chapters bear the following titles: Fundamental Principles; Classification of the Elements; The Electron Theory; Gases; Liquids; Solids; Solutions; Dilute Solutions and Osmotic Pressure; Association, Dissociation and Solvation; Colloidal Solutions; Thermochemistry; Homogeneous Equilibrium; Heterogeneous Equilibrium; Chemical Kinetics; Electrical Conductance; Electrolytic Equilibrium and Hydrolysis; Electromotive Force; Electrolysis and Polarization; Actinochemistry. As this list shows, the field is well covered; in each chapter there is a good selection of topics with well chosen illustrative examples and references to original sources. A collection of problems designed to test the student's grasp of the subject is found at the end of each chapter. It has been the author's aim, as announced in the preface, "to present the more difficult portions of the subject * * * in a clear and logical manner;" and, on the whole, in the opinion of the reviewer, he has been successful. Misprints are rare; the figures, of which there are more than one hundred, are good and the press work and binding are first-class.

While the presentation of most topics is good, there are some cases such as combining and atomic weights, p. 8; deduction of Avogadro's Law from the kinetic theory, p. 55; and the deduction of the Phase Rule, p. 290, where the treatment is weak. There are a few topics where the author seems to have forgotten that he is writing for beginners and that he should make the rough places smoother; thus on p. 72, in discussing the method of Clement and Desormes for the determination of the ratio of the two specific heats of a gas, the author speaks of an adiabatic expansion and uses the adiabatic equation relating pressure and volume, without a word of explanation regarding the nature of an adiabatic process or the derivation or significance of the equation he has used. On p. 195, in the deduction of the equation for the elevation of the boiling point, we read: "Applying the well known thermodynamic relation, that the ratio of the work done to the heat absorbed, is the same as the ratio of the difference in temperature to the absolute initial temperature of the system, we have," etc. While it is certainly proper in an advanced treatise or a journal paper to refer to the simplest statement of the second law as *well known*; it is equally certain that this fundamental relation is *not* well known to most students who are beginning the study of physical chemistry, nor will such find further light on this most important subject in this text, excepting in two places where the treatment is essentially the same as in the case mentioned.

While the author devotes a 13-page chapter very satisfactorily to the electron theory, there is nothing on radioactivity; but it does seem a pity that he did not take one page for one of the most brilliant, and to the chemists most interesting, of recent results of electron research, namely, the exact knowledge of the absolute weight of an atom, which follows at once from a knowledge of the charge of an electron. The value for the elementary electric charge given is the old one, 25% in error, which should be replaced by Millikan's new value, $e = 4.775 \times 10^{-10}$ E. S. U.

There are a number of loose, partial or erroneous statements which are open to criticism, as for example: p. 159, the definition of a saturated solution; p. 187, the statement of Babo's second law, which is meaningless as given; p. 274, the statement that the differential equation relating equilibrium constant and temperature can "only be integrated if Q is constant." The student does not learn from the book that the fundamental problem is to find Q as a function of the temperature and thus secure a general solution of the problem. On p. 329, we find the classic statement that "the equilibrium is not disturbed by the presence of a catalyst." In the light of the important work of Bredig, of Stieglitz and of Acree on catalysis, this dictum can no longer be considered as more than approximate in many cases. Contrary to the statement found on p. 209, an aqueous solution of chlorine does precipitate silver nitrate; according to Jakowin[1] this is due to the reaction: $Cl_2 + H_2O \rightleftarrows HCl + HClO$.

But these defects, which it is the duty of the reviewer to point out, do not, by any means, spoil this carefully written book. *Ideal* text books are like ideal gases: very often discussed but never realized. Let us at least hope that as text follows text we are approaching *The Ideal* asymptotically!

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[1] *Z. phys. Chem.*, 29, 613.

HERBERT N. McCOY.

Monographs on Inorganic and Physical Chemistry. Edited by ALEXANDER FINDLAY. **The Viscosity of Liquids.** A. E. DUNSTAN AND F. B THOLE. Longmans, Green & Co. vi + 91 pp. Price, 90 cents.

This volume brings together in compact and very readable form the results of a large amount of work on viscosity. To select material from the thousand or more papers on this subject, representing many thousands of pages of material for a volume of so small a compass, must have been a serious task. The working principle, Findlay states in his preface to the series, is to give "to those engaged in guiding the reading of advanced students of chemistry adequately summarized accounts of the progress made in recent years." The authors, therefore, discuss at length the problems now pressing for solution, stated in their preface, p. v., as follows: "In spite of a century of experimental work no very definite method has been set up for the measurement of viscosity, and no general agreement has been arrived at for the setting forth and interpretation of the results obtained." So clear a statement leaves no doubt as to the importance of the problems and in itself brings nearer the solution. The discussion of these problems is admirable.

However, in this method of presentation one wonders whether the student will be able to get the right perspective when the problems which have been satisfactorily solved in the past receive so slight attention. For example, the authors give considerable space to the discussion of the different instruments for measurement by transpiration. But they do not refer to the discussion which ran in the literature during the middle of the last century over the fact that the transpiration method of Poiseuille gave results which failed to agree with those obtained by the older method of Coulomb. It was finally satisfactorily proved that when the proper corrections are made both of the above methods, as well as other new methods, give concordant results, although the transpiration method is the most convenient and reliable. So the discussion today is after all merely as to the form of transpiration apparatus which will most conveniently give reliable results. It is important for the student to know that the absolute transpiration method is definite in the sense that its results are reproducible, the necessary corrections, the methods for obtaining the dimensions of the apparatus, as well as the nature of the flow being fairly well understood. The discussion at present arises from the fact that absolute measurements are not always convenient and relative measurements and are not always reliable.

The monograph is free from typographical errors and any other errors

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